ANUÁRIO CIENTÍFICO 2003

Resumos de Artigos, Comunicações, Teses e Livros

INSTITUTO SUPERIOR DE ENGENHARIA DE LISBOA

FICHA TÉCNICA

Edição
Conselho Científico do Instituto
Superior de Engenharia de Lisboa
Rua Conselheiro Emídio Navarro, nº 1
1949-014 Lisboa
Tel. 21 831 70 10
Fax 21 831 70 09

Capa e Layout
O Gabinete - Design de Comunicação
Tel 21 443 66 56
ogabinete@netcabo.pt

Produção Gráfica
Aço Artes Gráficas
Tel 21 361 76 80
acografica@acografica.pt

Tiragem
1000 Exemplares

Data
2004

ÍNDICE

Anuário Científico 2003
ISEL

NOTA INTRODUTÓRIA

O Conselho Científico do Instituto Superior de Engenharia de Lisboa dá continuidade à publicação do Anuário Científico do ISEL com esta edição relativa ao ano de 2003.

O Instituto Superior de Engenharia de Lisboa tem vindo a dar o seu contributo ao desenvolvimento do país, quer através da formação de engenheiros, quer através da prestação de serviços à comunidade, sem esquecer as funções de disseminação de conhecimentos e de transferência de tecnologia, que também lhe competem e que este anuário demonstra.

O ISEL possui cursos acreditados pelas associações profissionais, Ordem dos Engenheiros e Associação Nacional dos Engenheiros Técnicos, em todas as suas áreas de formação.

Os conhecimentos científicos são o suporte das competências do Engenheiro que lhe permitem utilizar, adequadamente, as tecnologias disponíveis.

Ciência e investigação são indissociáveis e imprescindíveis numa escola de engenharia. Este binómio está, muitas vezes, directa ou indirectamente, ligado à realização de teses de mestrado e de doutoramento.

Continuamos a insistir na necessidade de levar o poder político a compreender que a qualidade do engenheiro não depende do subsistema de ensino superior, mas sim da qualidade da escola de engenharia que o formou. Vem sendo notória, quer pelos trabalhos desenvolvidos, quer pelo nível académico do seu corpo docente, a competência do ISEL para a concessão dos graus de pós-graduação.

Reafirmamos a nossa convicção neste propósito e na necessidade de ultrapassar o espartilho legal que o constrange, continuando empenhados em dar o nosso melhor contributo à sociedade.

O Presidente do Conselho Científico

Elmano Margato

(Prof. Elmano Margato)

QUALIDADE EM PORTUGAL: QUE FUTURO?

Pedro Mendonça
Instituto Superior de Engenharia de Lisboa
pedro.mendonca@netcabo.pt
dec@dec.isel.ipl.pt

Publicado em: *Revista Recursos Humanos Magazine no nº de Janeiro/Fevereiro 2003*

As exigências do novo padrão de competitividade, obrigam a uma grande mudança de mentalidades: grande esforço em matéria de educação de base da população, de formação profissional, de interacção entre as empresas e o novo sistema de investigação e desenvolvimento e de capacidade de pôr de pé projectos empresariais assentes na inovação, na qualidade e numa capacidade diferente de relacionamento, com os mercados.

Tudo o resto (máquinas, métodos, materiais) se pode comprar ou copiar.

As armas serão a qualidade, o serviço ao cliente, a rapidez de resposta, a inovação, a criação de marcas, o *design*, o *just in time*, a diversificação.

Como é que se "vende" ao mercado esta preocupação de urgência em atacar esta realidade?

Como conseguir que as empresas se especializem em qualidade, quando temos baixos níveis de formação em gestão para os dirigentes e quadros intermédios e muito baixos níveis de instrução para os executantes?

Como conseguir que as empresas percebam que têm de investir na formação, se sintam estimuladas para aprender a aprender e façam “crescer” os colaboradores?

Como conseguir que as empresas se adaptem aos novos desafios do paradigma das *TI*?

Como conseguir que se encurte a distância hierárquica e aumente o envolvimento dos colaboradores, para assim se obterem melhorias sustentadas e progressivas de qualidade?

O artigo procura responder a estas questões.

MONITORIZAÇÃO E MODELAÇÃO DO COMPORTAMENTO DINÂMICO DE BARRAGENS DE BETÃO.

S. Oliveira,[a] J. Rodrigues,[b] P. Mendes,[c] A. Campos Costa[b]

[a]Departamento de Barragens, LNEC, Lisboa, Portugal
[b]Departamento de Estruturas, LNEC, Lisboa, Portugal
[c]Departamento de Engenharia Civil, ISEL, Lisboa, Portugal

Publicado em: *Livro de Comunicações do XVII Congresso de Mecânica Aplicada e Computacional, Abril de 2003.*

Neste trabalho pretende-se mostrar que os recentes desenvolvimentos ao nível dos equipamentos de medição de vibrações e ao nível das metodologias de identificação modal, possibilitam o desenvolvimento de sistemas de monitorização dinâmica para grandes barragens, que permitirão registar e analisar continuamente, com uma precisão aceitável, a resposta dinâmica destas obras sob a acção do ruído ambiente e sob acções sísmicas de diferentes intensidades. Salienta-se que, no âmbito das actividades de controlo da segurança de barragens, estes sistemas poderão ter grande interesse, nomeadamente: i) na análise de processos de deterioração evolutiva; e ii) na análise dos efeitos das acções sísmicas. Apresentam-se resultados de medições dinâmicas efectuadas na barragem do Cabril, sob a acção da excitação ambiente, os quais são comparados com resultados de anteriores medições realizadas em ensaios de vibração forçada. Os resultados observados são comparados com os de um modelo numérico de elementos finitos tridimensionais baseado na hipótese de comportamento elástico linear admitindo que o efeito hidrodinâmico da água é adequadamente simulado através de massas de água associadas segundo a fórmula de Westergaard.

PAREDES ESTUCADAS EM EDIFÍCIOS ANTIGOS

Paulo Malta da Silveira[a]; Rosário Veiga[b]; Jorge de Brito[c]

[a] Instituto Superior de Engenharia de Lisboa; [b] Laboratório Nacional de Engenharia Civil; [c] Instituto Superior Técnico

Publicado em: *3.º ENCORE - Encontro sobre Conservação e Reabilitação de Edifícios, LNEC, Lisboa, 26 a 30 de Maio de 2003.*

Os edifícios antigos encerram um conjunto de informação relativo aos materiais e aos processos construtivos tradicionais. A perda deste património dificulta o estudo dos edifícios antigos, nomeadamente o diagnóstico patológico e a escolha de soluções de conservação ou reparação. Na presente comunicação recuperou-se algo deste conjunto de informação relativo aos estuques antigos, em especial quanto ao seu mais importante suporte - as paredes. Apresenta-se pois uma breve descrição do modo de execução dos diferentes tipos de paredes que eram habitualmente estucadas: as paredes de alvenaria, os frontais, e os tabiques. Caracteriza-se também a forma de execução do fasquiado, e por fim a constituição das diferentes camadas do revestimento estucado: o reboco, o esboço e o estuque.

CONTROLO DA QUALIDADE DA CONSTRUÇÃO DO ATERRO SANITÁRIO DE VILA NOVA DE GAIA E STª MARIA DA FEIRA

M. G. Lopes

Laboratório Nacional de Engenharia Civil; Instituto Superior de Engenharia de Lisboa

Publicado em: *Relatório LNEC nº 306/03-NP, LNEC, Lisboa, Julho de 2003.*

A gestão de resíduos e, nomeadamente, dos resíduos sólidos urbanos (RSU), teve um grande impulso e desenvolvimento a partir da aprovação, em Novembro de 1996, do Plano Estratégico de Gestão de Resíduos Sólidos Urbanos (PERSU) que apresenta, como grandes linhas de acção, o encerramento das lixeiras, a sua substituição por infra-estruturas adequadas de confinamento em aterro e o desenvolvimento de redes de recolha selectiva.

Neste contexto, foram identificados os responsáveis pela gestão dos RSU e definida a distribuição dos novos sistemas de gestão de RSU. Em 1997 estavam criados 29 sistemas municipais, cuja gestão, podia ser concessionada a qualquer entidade pública ou privada de natureza empresarial, e 11 sistemas multimunicipais, cuja gestão e exploração foi concessionada a empresas de capitais maioritariamente públicos, designadamente a Empresa Geral de Fomento e as autarquias.

As empresas concessionárias dos sistemas multimunicipais de Vale do Minho (VALORMINHO), Vale do Lima e Baixo Cavado (RESULIMA), Baixo Cavado (BRAVAL), Gaia e Feira (SULDOURO), Alta Estremadura (VALORLIS), Litoral Centro (ERSUC) e Algarve (ALGAR), responsáveis pelos processos de concurso para a concepção e construção dos aterros sanitários de Valença, Viana do Castelo, Braga, Vila Nova de Gaia, Leiria, Aveiro e Figueira da Foz, Barlavento e Sotavento, pediram, em 1997, ao Laboratório Nacional de Engenharia Civil (LNEC) um estudo sobre a Avaliação da Qualidade de Aterros Sanitários de Resíduos Sólidos Urbanos, que incluía, numa primeira fase, a apreciação dos projectos e, numa segunda fase, o controlo da qualidade da construção, dos referidos aterros.

Relativamente à primeira fase da assessoria prestada pelo LNEC à empresa SULDOURO – Valorização e Tratamento de Resíduos Sólidos, S.A., no âmbito da apreciação técnica do Projecto do Aterro Sanitário de

Vila Nova de Gaia e ST^{a} Maria da Feira, foi elaborado um relatório com dois volumes, onde foi referido o acompanhamento técnico da elaboração do projecto na sua componente ambiental (volume 1) e geotécnica (volume 2).

Neste relatório são resumidas as actividades geotécnicas desenvolvidas pelo LNEC relativamente à segunda fase da assessoria prestada pelo LNEC à empresa SULDOURO – Valorização e Tratamento de Resíduos Sólidos, S.A., no âmbito do controlo da qualidade da construção do Aterro Sanitário de Vila Nova de Gaia e ST^{a} Maria da Feira.

ACOMPANHAMENTO DO PROJECTO DE EXECUÇÃO DO ATERRO SANITÁRIO DE VILA NOVA DE GAIA E Stª MARIA DA FEIRA. VOLUME 2- COMPONENTE GEOTÉCNICA

M. G. Lopes
Laboratório Nacional de Engenharia Civil; Instituto Superior de Engenharia de Lisboa

Publicado em: *Relatório LNEC nº 311/03-NP, LNEC, Lisboa, Julho de 2003.*

A gestão de resíduos e, nomeadamente, dos resíduos sólidos urbanos (RSU), teve um grande impulso e desenvolvimento a partir da aprovação, em Novembro de 1996, do Plano Estratégico de Gestão de Resíduos Sólidos Urbanos (PERSU) que apresenta, como grandes linhas de acção, o encerramento das lixeiras, a sua substituição por infra-estruturas adequadas de confinamento em aterro e o desenvolvimento de redes de recolha selectiva.

Neste contexto, foram identificados os responsáveis pela gestão dos RSU e definida a distribuição dos novos sistemas de gestão de RSU. Em 1997, estavam criados 29 sistemas municipais, cuja gestão, podia ser concessionada a qualquer entidade pública ou privada de natureza empresarial, e 11 sistemas multimunicipais, cuja gestão e exploração foi concessionada a empresas de capitais maioritariamente públicos, designadamente a Empresa Geral de Fomento e as autarquias.

As empresas concessionárias dos sistemas multimunicipais de Vale do Minho (VALORMINHO), Vale do Lima e Baixo Cavado (RESULIMA), Baixo Cavado (BRAVAL), Gaia e Feira (SULDOURO), Alta Estremadura (VALORLIS), Litoral Centro (RESUC) e Algarve (ALGAR), responsáveis pelos processos de concurso para a concepção e construção dos aterros sanitários de Valença, Viana do Castelo, Braga, Vila Nova de Gaia, Leiria, Aveiro e Figueira da Foz, Barlavento e Sotavento, pediram, em 1997, ao Laboratório Nacional de Engenharia Civil (LNEC) um estudo sobre a Avaliação da Qualidade de Aterros Sanitários de Resíduos Sólidos Urbanos, que incluía, numa primeira fase, a apreciação dos projectos e, numa segunda fase, o controlo de qualidade da construção, dos referidos aterros.

Relativamente à primeira fase da assessoria prestada pelo LNEC à empresa SULDOURO – Valorização e Tratamento de Resíduos Sólidos, S.A., da apreciação técnica do Projecto do Aterro Sanitário de Vila Nova de Gaia e ST^a Maria da Feira foi elaborado um relatório com dois volumes.

No Volume 1 foi referido o acompanhamento técnico da elaboração do projecto na sua componente ambiental, designadamente, de drenagem e tratamento de lixiviados, de produção de gases do aterro, das incidências ambientais e dos aspectos de exploração e de monitorização no domínio das águas subterrâneas. Neste Volume 2 são resumidas as actividades desenvolvidas pelo LNEC no âmbito da apreciação geotécnica do projecto e indicadas as medidas suplementares ou correctivas que se afiguraram necessárias à garantia de qualidade da infra-estrutura a construir e do seu desempenho na fase de exploração.

NEW STUDY OF THE 1755 EARTHQUAKE SOURCE BASED ON MULTI-CHANNEL SEISMIC SURVEY DATA AND TSUNAMI MODELLING

M. A. Baptista,[a,b]., J.M. Miranda[b], F. Chiericci[c], N. Zitellini[4]

[a] Instituto Superior de Engenharia de Lisboa mabaptista@sa.isel.ipl.pt
[b]Centro de Geofísica da Universidade de Lisboa, Portugal
[c] Instituto de Radioastronomia, Matera, Itália
[d] Instituto di Geologia Marina, Via Gobeti, Bologna, Italia

Publicado em: *Natural Hazards and Earth Science Systems,3,:1-8 European Geosciences Union 2003.*

Abstract. In the last years, large effort has been done to carry out multi-channel seismic reflection surveys (MCS) in SW Iberia to locate the active tectonic structures that could be related to the generation of the 1755 Lisbon earthquake and the tsunami. The outcome of these researches led to the identification of a large, compressive tectonic structure, named Marquês de Pombal thrust that, alone can account for only half the seismic energy released by the 1755 event. However, these investigation have shown the presence of additional tectonic structures active along the continental margin of SW Iberia that are here evaluated to model the tsunami waves observed along the coasts of Iberia, Morocco and Central Atlantic. In this paper we present a new reappraisal of the 1755 source, proposing a possible composite source, including the Marquês de Pombal thrust fault and the Guadalquivir Bank. The test of the source is achieved through numerical modelling of the tsunami all over the North Atlantic area. The results presented now incorporate data from the geophysical cruises and the historical observation along the European coasts and also from the Western Indies. The results of this study will, hopefully, improve the seismic risk assessment and evaluation in the Portuguese territory, Spain, Morocco and Central/North Atlantic

GEOTECHNICAL ASPECTS AND CONSTRUCTION QUALITY ASSURANCE PLANS FOR MSW LANDFILLS RECENTLY BUILT IN PORTUGAL.

F Pardo de Santayana, [a]; M. G. Lopes [b]

[a]Laboratório Nacional de Engenharia Civil, LNEC, Lisboa, Portugal E-mail: fpardo@lnec.pt
[b]Departamento de Engenharia Civil, ISEL, Lisboa, Portugal E-mail: glopes@dec.isel.ipl.pt

Publicado em: *Livro de Resumos do 13 Congres European des Sols et de la Geotechnique, Praga, República Checa, 25 a 28 de Agosto de 2003.*

The paper describes some results of the activities of the Laboratório Nacional de Engenharia Civil (LNEC) related to the implementation of CQA plans and provision of geotechnical advice for the recently built MSW Portuguese landfills. Reference is made to different geotechnical problems arisen during construction, including short descriptions of case histories where slope stability problems came up affecting either the excavation or the constructed slopes.

O SISTEMA DE ENSINO/FORMAÇÃO NO SÉCULO XXI

Pedro Mendonça

Instituto Superior de Engenharia de Lisboa
pedro.mendonca@netcabo.pt
dec@dec.isel.ipl.pt

Publicado em: Comunicação incluída no Seminário promovido pelo Instituto de Defesa Nacional em Outubro de 2003, sob o Tema "Educação, Liberdade e Cidadania".

Resumo

Os desafios impostos pela globalização, pelas tecnologias da informação e pelo ambiente obrigam a respostas por parte do Sistema de Ensino/Formação: a maneira de ensinar e de aprender da Era Industrial tem de ser adaptada às novas exigências da Era do Conhecimento.

DAMAGE DETECTION IN CONCRETE DAMS USING DYNAMIC CONTINOUS MONITORING.

S. Oliveira,[a] J. Rodrigues,[b] P. Mendes,[c] A. Campos Costa[b]

[a]Departamento de Barragens, LNEC, Lisboa, Portugal
[b]Departamento de Estruturas, LNEC, Lisboa, Portugal
[c]Departamento de Engenharia Civil, ISEL, Lisboa, Portugal

Publicado em: *Livro de Comunicações do 9th International Conference and Promotion of Computational Methods in Engineering and Science, Novembro de 2003.*

Ever since various decades LNEC has been trying to identify the processes of evolutive deterioration in concrete structures, namely in concrete dams, by establishing a correlation between the modal parameters (natural frequencies and modal configurations), which refer to the dynamic structural behaviour, and the deterioration of the structural characteristics. The experience obtained by LNEC, in various forced vibration tests in concrete dams, makes it possible to conclude that the intended objective cannot be reached on the basis of measurements with 5-to-10 year intervals. In fact, the modal parameters to be identified are influenced not only by the deterioration of the structure over time, but also by the environmental thermal variations and by the variations in the reservoir water level. Therefore, it is necessary to measure the dynamic response using new systems for continuous dynamic monitoring, using only the vibrations in the dams under operational conditions. This derives from the need to obtain histories of evolution of the modal parameters over time, in accordance with: thermal variations, with variations in the reservoir water level and, obviously, with time dependent effects.

This work presents the results of dynamic measurements carried out at Cabril dam (the highest Portuguese arch dam: 132 m of maximum height), under the action of environmental excitation, which are compared with results from previous measurements carried out in forced vibration tests. The observed results are compared with those of a 3D finite element model. It is discussed the influence of reservoir water levels and of the thermal state on the time evolution of the fundamental parameters of the dynamic response, as well as the influence of the deterioration effects on those same parameters.

NEW SIMULATION OF THE 1755 TSUNAMI SOURCE USING A COMPOSITE SUBDUCTION

M. A. Baptista,[a,b] , M. A.Gutscher[c] ,J.M. Miranda[a]

[a] Instituto Superior de Engenharia de Lisboa mabaptista@sa.isel.ipl.pt
[b]Centro de Geofísica da Universidade de Lisboa, Portugal
[c] IUM, Université de Bretagne Occidentale, France

Publicado em: *EosTrans. AGU, 84*(46), Fall Meet. Suppl., Abstract, San Francisco, USA, Dec 2003

A recent marine seismic survey, together with tomographic data, provides compelling evidence for an active east dipping subduction zone beneath the Gibraltar Arc, which can be thought as a candidate for the 1755 Lisbon earthquake. If we consider a convergent rate of 1 to 2 cm/yr and a co-seismic slip of 20 m (to account for the 1755 earthquake magnitude), we get a recurrence interval between 1000 and 2000 years, that seems compatible with available geological information. Previous attempts to model the tsunami wave that could be generated by such structure concluded that synthetic amplitudes are lower and arrival times longer than observed, particularly for locations along the west coast of Portugal. This suggested a second source segment, closer to the Portuguese margin, which should have also contributed to the tsunami waves that ravaged the coast of SW Portugal and the Gulf of Cadiz, and were reported as far as the Lesser Antilles and SW England. This possibility is also reinforced by some historic documents that report the occurrence of at least a second large shock. In this paper we present the simulation of a composite 1755 source, where the main shock is attributed to dipping subduction beneath the Gibraltar Arc, modelled as a 180 km (N-S) x 210 km (E-W) rectangular fault with a 20 m co-seismic slip, followed by a second shock, 10 minutes later, beneath the southern flank of Gualdalquivir Bank, modelled as a 250 km (WNW-ESE) x 71 km (WSW-ESE) rectangular fault with 5 m co-seismic slip. Tsunami wave heights are computed for all locations where reliable historical information is available and comparison is made between synthetic values and observations.

CONTROLO DA QUALIDADE DA CONSTRUÇÃO DO ATERRO SANITÁRIO DE AVEIRO

M. G. Lopes
Laboratório Nacional de Engenharia Civil; Instituto Superior de Engenharia de Lisboa

Publicado em: Relatório *LNEC nº 388/03-NP, LNEC, Lisboa, Dezembro de 2003.*

A gestão de resíduos e, nomeadamente, dos resíduos sólidos urbanos (RSU), teve um grande impulso e desenvolvimento a partir da aprovação, em Novembro de 1996, do Plano Estratégico de Gestão de Resíduos Sólidos Urbanos (PERSU) que apresenta, como grandes linhas de acção, o encerramento das lixeiras, a sua substituição por infra-estruturas adequadas de confinamento em aterro e o desenvolvimento de redes de recolha selectiva.

Neste contexto, foram identificados os responsáveis pela gestão dos RSU e definida a distribuição dos novos sistemas de gestão de RSU. Em 1997 estavam criados 29 sistemas municipais, cuja gestão, podia ser concessionada a qualquer entidade pública ou privada de natureza empresarial, e 11 sistemas multimunicipais, cuja gestão e exploração foi concessionada a empresas de capitais maioritariamente públicos, designadamente a Empresa Geral de Fomento e as autarquias.

As empresas concessionárias dos sistemas multimunicipais de Vale do Minho (VALORMINHO), Vale do Lima e Baixo Cavado (RESULIMA), Baixo Cavado (BRAVAL), Gaia e Feira (SULDOURO), Alta Estremadura (VALORLIS), Litoral Centro (ERSUC) e Algarve (ALGAR), responsáveis pelos processos de concurso para a concepção e construção dos aterros sanitários de Valença, Viana do Castelo, Braga, Vila Nova de Gaia, Leiria, Aveiro e Figueira da Foz, Barlavento e Sotavento, pediram, em 1997, ao Laboratório Nacional de Engenharia Civil (LNEC) um estudo sobre a Avaliação da Qualidade de Aterros Sanitários de Resíduos Sólidos Urbanos, que incluía, numa primeira fase, a apreciação dos projectos e, numa segunda fase, o controlo da qualidade da construção, dos referidos aterros.

Relativamente à primeira fase da assessoria prestada pelo LNEC à empresa ERSUC –Resíduos Sólidos do Centro, S.A, no âmbito da apreciação técnica do Projecto do Aterro Sanitário de Aveiro, foi elaborado um relatório com dois volumes, onde foi referido o acompanhamento técnico da elaboração do projecto na sua componente ambiental (volume 1) e geotécnica (volume 2).

Neste relatório são resumidas as actividades geotécnicas desenvolvidas pelo LNEC relativamente à segunda fase da assessoria prestada pelo LNEC à empresa ERSUC –Resíduos Sólidos do Centro, S.A, no âmbito do controlo da qualidade da construção do Aterro Sanitário de Aveiro.

ACOMPANHAMENTO DO PROJECTO DE EXECUÇÃO DO ATERRO SANITÁRIO DE AVEIRO. VOLUME 2- COMPONENTE GEOTÉCNICA

M. G. Lopes
Laboratório Nacional de Engenharia Civil; Instituto Superior de Engenharia de Lisboa

Publicado em: *Relatório LNEC nº 387/03-NP, LNEC, Lisboa, Dezembro de 2003.*

A gestão de resíduos e, nomeadamente, dos resíduos sólidos urbanos (RSU), teve um grande impulso e desenvolvimento a partir da aprovação, em Novembro de 1996, do Plano Estratégico de Gestão de Resíduos Sólidos Urbanos (PERSU) que apresenta, como grandes linhas de acção, o encerramento das lixeiras, a sua substituição por infra-estruturas adequadas de confinamento em aterro e o desenvolvimento de redes de recolha selectiva.

Neste contexto, foram identificados os responsáveis pela gestão dos RSU e definida a distribuição dos novos sistemas de gestão de RSU. Em 1997, estavam criados 29 sistemas municipais, cuja gestão, podia ser concessionada a qualquer entidade pública ou privada de natureza empresarial, e 11 sistemas multimunicipais, cuja gestão e exploração foi concessionada a empresas de capitais maioritariamente públicos, designadamente a Empresa Geral de Fomento e as autarquias.

As empresas concessionárias dos sistemas multimunicipais de Vale do Minho (VALORMINHO), Vale do Lima e Baixo Cavado (RESULIMA), Baixo Cavado (BRAVAL), Gaia e Feira (SULDOURO), Alta Estremadura (VALORLIS), Litoral Centro (ERSUC) e Algarve (ALGAR), responsáveis pelos processos de concurso para a concepção e construção dos aterros sanitários de Valença, Viana do Castelo, Braga, Vila Nova de Gaia, Leiria, Aveiro e Figueira da Foz, Barlavento e Sotavento, pediram, em 1997, ao Laboratório Nacional de Engenharia Civil (LNEC) um estudo sobre a Avaliação da Qualidade de Aterros Sanitários de Resíduos Sólidos Urbanos, que incluía, numa primeira fase, a apreciação dos projectos e, numa segunda fase, o controlo de qualidade da construção, dos referidos aterros.

Relativamente à primeira fase da assessoria prestada pelo LNEC à empresa ERSUC –Resíduos Sólidos do Centro S.A., da apreciação técnica do Projecto do Aterro Sanitário de Aveiro foi elaborado um relatório com dois volumes.

No Volume 1 foi referido o acompanhamento técnico da elaboração do projecto na sua componente ambiental, designadamente, de drenagem e tratamento de lixiviados, de produção de gases do aterro, das incidências ambientais e dos aspectos de exploração e de monitorização no domínio das águas subterrâneas. Neste Volume 2 são resumidas as actividades desenvolvidas pelo LNEC no âmbito da apreciação geotécnica do projecto e indicadas as medidas suplementares ou correctivas que se afiguraram necessárias à garantia de qualidade da infra-estrutura a construir e do seu desempenho na fase de exploração.

MÁQUINA ELÉCTRICA ROTATIVA PARA UMA SUSPENSÃO ELECTROMAGNÉTICA

Paulo José Duarte Landeiro Gambôa

Mestrado em: *Engenharia Electrotécnica e de Computadores.*

Grau Concedido por: *IST – Universidade Técnica de Lisboa.*

Orientadores: *Doutor Jorge Manuel Garcia Esteves (orientador científico e Professor Auxiliar do IST) e Doutor Elmano da Fonseca Margato (co-orientador científico e Professor Coordenador do ISEL).*

Provas Concluídas em: *6 de Junho de 2003.*

O desenvolvimento dos materiais ferromagnéticos, da electrónica de potência e das técnicas de controlo, permite a construção e o controlo de actuadores electromagnéticos de pequenas dimensões e considerável força. A redução das perdas por atrito e a grande flexibilidade destes actuadores permitem a sua aplicação em suspensões automóveis do tipo activo, tendo-se obtido duas novas topologias: a suspensão levitante e a pseudo-levitante. Neste trabalho apresenta-se uma lei de controlo para a suspensão pseudo-levitante, a qual possui o objectivo de assegurar, simultaneamente, a minimização da aceleração da massa suspensa (perspectiva do conforto) e a manutenção, dentro dos limites aceitáveis, da deformação do pneu (perspectiva de segurança). Considera-se, que a solução do actuador electromagnético pode assumir, na sua construção, uma topologia linear de raiz, ou ser constituído por uma máquina eléctrica rotativa com um sistema de conversão de movimento rotativo em linear. Com o objectivo de confirmar os resultados teóricos relativos ao estudo da utilização de máquinas eléctricas rotativas em suspensões activas, apresentam-se os correspondentes resultados experimentais, obtidos a partir de uma bancada de ensaios utilizada para este efeito. A bancada de ensaios utilizada na obtenção dos resultados experimentais é composta por dois accionamentos electromecânicos. Um dos accionamentos funciona como elemento actuador e simula o comportamento da máquina eléctrica rotativa na suspensão activa proposta. O outro accionamento funciona como elemento perturbador e reproduz, sobre o elemento actuador, a acção dinâmica dos restantes componentes da suspensão.

INTEGRAÇÃO DE MERCADOS DE ENERGIA ELÉCTRICA - Implicações nos lucros das empresas produtoras, no excedente dos consumidores e no bem estar social

J. Sousa

Departamento de Engenharia Electrotécnica e Automação, ISEL, Lisboa, Portugal

Publicado em: *Proceedings do 6º Encontro Nacional do Colégio de Engenharia Electrotécnica da Ordem dos Engenheiros, Lisboa, Portugal, Maio 2003.*

A liberalização do sector eléctrico introduz a possibilidade de escolha por parte dos consumidores e produtores das condições em que efectuam as transacções de energia eléctrica. Num ambiente não competitivo a produção e os preços são regulados, enquanto que nas actividades liberalizadas a regulação económica visa essencialmente evitar o abuso de poder de mercado. Neste sentido a competição entre produtores deve ser promovida como forma de aumentar a eficiência económica, sendo a integração de mercados uma forma de alcançar este objectivo. Tendo em consideração a integração e total liberalização dos mercados de electricidade de Portugal e Espanha, dando origem ao Mercado Ibérico de Electricidade (MIBEL) em 2004, são apresentadas algumas implicações económicas da integração de dois mercados. Num contexto de equilíbrio parcial e à luz de um modelo de oligopólio de Cournot determinam-se os equilíbrios em ambos mercados, quando separados, e no mercado resultante, após a integração. Das várias conclusões apresentadas no presente estudo evidenciam-se o acréscimo do bem estar social, a redução do preço de equilíbrio, o consequente aumento do excedente dos consumidores e a diminuição no lucro total das empresas, em termos comparativos entre o mercado integrado e o conjunto dos dois mercados quando separados.

AN EXPERIMENTAL APPROACH TO TEACHING CONTROL SYSTEMS IN ELECTRICAL ENGINEERING

Joaquim Soares, Luís Encarnação
Departamento de Engenharia Electrotécnica e Automação, ISEL, Lisboa, Portugal

Publicado em: *8.º CLEEE - Congresso Luso Espanhol de Engenharia Electrotécnica, Vilamoura, Portugal, Julho de 2003*

Experimental training is fundamental in engineering sciences, especially in those involving technologies. An important factor in engineering training consists in establishing coherence between theoretical concepts (physical analysis and mathematical modeling) and practice (components, devices and industrial equipment). Software simulation has been of great help for training and exercising in order to achieve useful skills in control systems, usually at moderate cost and great flexibility. However, further contact with physical equipment is also required. Hardware simulation and hybrid simulation are better suited for this purpose, but still have limitations. Work with industrial equipment is the ultimate goal for an engineer. Thus the teaching effort should also be focused on this matter, without loosing the connection with theoretical concepts. The attempt to find appropriate processes to be controlled for the laboratory has to discard expensive, bulky, dangerous and too complex systems. Controller types have to match solutions studied in theory (linear systems modeled with transfer functions) and cover the most up to date technologies that can be found in practice. For electrical engineering students a close contact with the analogue electronics (at component level) is required. Then other (black box) industrial controllers should be tackled, namely, industrial PID controller and programmable logic controller. The present attempt consists of using a real system, e.g. a small electrically heated stove as the process to be controlled, and developing control solutions successively with three kinds of controllers technology: analogue electronics assembled in breadboard, industrial parametrisable PID controller and programmable logic controller which are the most commonly used controller equipments. Merits and limitations of these controllers are discussed.

AN ELECTRONIC VOTING SYSTEM

N. Pedro[a], J. Palma[ab]

[a]Departamento de Engenharia Electrotécnica e Automação e Centro de Electrotecnia e Electrónica Industrial, ISEL, Portugal
[b]Centro de Instrumentação Científica, LNEC, Portugal

Publicado em: *Actas do 8º Congresso Luso-Espanhol de Engenharia Electrotécnica, Vilamoura, Portugal, Julho de 2003.*

The conception of an electronic voting system for small assemblies (up to 64 members) is described. It was developed as a low cost solution based on serial bus data transmission at short distances. Each individual voting console has an Intel 8751 microcontroller, an alphanumeric display and three buttons. Allusion is made to the essential characteristics of communication hardware and protocol, which were designed to achieve adequate reliability as confirmed with a prototype.

ELECTRIC MACHINES TEST BENCH AND ELECTROMAGNETIC AUTOMOTIVE SUSPENSION

Paulo Gambôa[a], Elmano Margato[a], Jorge Esteves[b],

[a]Departamento de Engenharia Electrotécnica e de Automação, ISEL, Lisboa, Portugal,

[b]Instituto Superior Técnico, IST, Lisboa, Portugal, E-mail: jorge.esteves@ist.utl.pt

Publicado em: *Actas do 8º Congresso Luso Espanhol de Engenharia Electrotécnica, Vilamoura, Portugal, Julho de 2003.*

The primary function of vehicle suspension is to isolate the vehicle body and passengers from the oscillations created by the road irregularities and produce a continuous road-wheel contact assuring security. Typically, current automobiles use passive suspensions where performance is reasonable but oscillations are only reduced. An alternative is to use active suspensions; however, due to the cost and energy consumption, it is only used in top models from cars manufacturers. Use of electromagnetic actuators can be a solution for solving the problem: to use linear electromagnetic actuators applied directly in the system or to use a rotating electric machine with a rotation transformation into linear movement. As a first approach to the implementation of this last alternative, a classical test bench with two electric drives was used (one drive simulating the actuator system in test and the other actuating as disturbance element) allowing to implement a position controller able to answer to the disturbance torque for different control algorithms, that after could be implemented in the vehicle electromagnetic suspension system.

HIGH VOLTAGE POWER SUPPLY FOR POLLUTANTS TREATMENT

Acácio Galhardo[a], Nuno Pinhão[b]

[a]Departamento de Engenharia Electrotécnica e de Automação, ISEL, Lisboa, Portugal,
[b]Instituto Tecnológico e Nuclear, Sacavém, Portugal, E-mail: npinhao@itn.mces.pt

Publicado em: *Actas do 8º Congresso Luso Espanhol de Engenharia Electrotécnica, Vilamoura, Portugal, Julho de 2003.*

The use of non-thermal plasma to treat exhaust gas is becoming more and more interesting for future industrial application. Producing the necessary high voltage and energy, at a very low cost and in field conditions, is mandatory for the success and spreading of this process and technology. The good efficiency of switched mode amplifiers point to their application for industrial production in ready to use equipment. This paper refers to the use of low cost switch mode power amplifiers and step-up transformers, connected to the plasma reactor high capacitance. The process to achieve the necessary variable voltage and frequency, up to 50 kHz and up to 20 kV, is discussed together the control and safety circuits. The capacitance of the reactor itself imposes certain rules and restrictions to be followed or to be avoided.

INTEGRATION OF ELECTRICITY MARKETS: IMPACTS ON POWER PRODUCER PROFITS, CONSUMER SURPLUS AND SOCIAL WELFARE

J. Sousa, V. Mendes,

Departamento de Engenharia Electrotécnica e Automação, ISEL, Lisboa, Portugal

Publicado em: *Proceedings do 8º Congresso Luso Espanhol de Engenharia Electrotécnica, Vilamoura, Portugal, Julho 2003.*

Until recently, power electricity systems were run by vertically integrated, typically state owned, monopolistic companies, comprising the generation, transmission, distribution and supply activities. This structure has been criticized on different grounds and reforms have taken place in many countries around the world.

Although different approaches are possible for these reforms, they often share a combination of full market opening, unbundling of transmission activities, regulated access to the network and liberalization of electricity trade.

The restructured environment is expected to increase the economic efficiency of the electricity industry, being the most significant impacts supposed to emerge in the long run, as a result of better investment decisions. In the short run, market structure is a key determinant of prices in the new electricity markets. In this respect, policy makers should pay attention to structural competition policies such as the opening of national markets to international trade. In this regard, it is of great interest to evaluate the impact of electricity market integration, such as the upcoming Iberian Electricity Market – MIBEL.

For this purpose, a model of Cournot oligopoly is employed to analyze the behaviour of firms in the two separate markets and in the integrated market. It is considered that all firms present the same technology and markets are alike. Under these conditions, it is shown that market integration is welfare improving increases consumers’ surplus and decreases power producers’ profits.

SHORT-TERM HYDRO SCHEDULE WITH HEAD-DEPENDENT. APPROACH BY A NON-LINEAR MODEL

S.J.P.S. Mariano[a], V.M.F. Mendes[b], L.A.F.M. Ferreira[c]

[a]Universidade da Beira Interior, Calçada Fonte do Lameiro, 6201-001 Covilhã, Portugal

[b]Instituto Superior de Engenharia, Avenida Emídio Navarro, 1950-062 Lisboa, Portugal

[c]Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal

Publicado em: *Proceedings do 8º Congresso Luso Espanhol de Engenharia Electrotécnica, Vilamoura, Portugal, Julho, 2003.*

In the present day electric liberalized energy framework, cost incurred by inferior planning is dragged away from costumers to power utilities, meaning less revenue for utilities. An unprecedented change, but a more bearable one, as always come natural to us that costumers should pay for everything, even for mistakes. Hence, to win the change, carrying a way an improved planning is absolutely crucial to build a strong tomorrow for a competitive utility power system.

In this framework, a utility with hydroelectric facilities faces the optimal tradeoff problem of how to make the present profit by the management of the water resources without compromise future potential profit in the electric energy market. This problem is known as the hydro-scheduling problem and it is usually divided in long-term problem and short-term problem. Normally, the long-term is stated as a stochastic problem, where as the short-term is state as a deterministic problem.

The short-term hydro-scheduling is the problem in advancing, during periods of one hour or half hour, the water release from reservoirs on basin of rivers to satisfy hydraulic constraints while achieving the best profit during the short-term horizon, normally one to seven days. A mathematical programming model with variable head is justified for improving the results of short-term hydro-schedule, particularly, in reservoirs where the head greatly depend on the volume of the stored water. In what follows the main features of our model for short-term hydro-schedule with head dependent is outlined briefly. Finally, a case study with three reservoirs is briefly discussed, illustrating the use and the success of our model.

SPECIAL REGULATIONS OF THE DEREGULATED MARKET.

N.A.S.Domingues[a], T.J.Gomes[a], D.Metz,[b] V.F.Mendes[c]

[a]Departamento de Engenharia Electrotécnica e Automação, ISEL, Lisboa, Portugal
[b]Centro de Energia Eléctrica da UTL, ISEL, Lisboa, Portugal
[c] Fachhochschule Darmstadt, Germany

Publicado em: *8º Congresso Luso-espanhol de Engenharia Electrotécnica, Julho 2003*

Usually power system engineers are trained to take care of the technical part of the power system, but now with the liberalization process taking place all over the world; new decision tools to improve technical skills are needed to face this process. Liberalization imposes a new philosophy, i.e., forces to reduce costs, to save money by increasing productivity so staff members and technical investments have been seriously reduced. Due to this philosophy a strong pressure to lower the staff labour costs came out. Obviously, power system engineers are responsible for decisions that can influence all power system investments and strongly affect the availability and security of the electrical power supply.

If failures or even emergency situations occur, they directly influence quality of power system supply. Hence, they influence the customers' feelings. Therefore, new tools are needed to overcome booth a reduction in staff labour and situations that influence customer's feelings. We studied regulation's penalties in different countries to keep good quality of the energy supply. We developed an application to compute the Compensation for Energy Not Supply to present economical indicators in a SCADA system. We present a case study using our application, showing how to improve technical skills based on economic indicators.

SHORT-TERM HYDRO SCHEDULING: A COMPARISON OF LINEAR WITH NON-LINEAR NETWORK MATHEMATICAL PROGRAMMING

J.P.S. Catalão[a], S.J.P.S. Mariano[a], V.M.F. Mendes[b], L.A.F.M. Ferreira[c]

[a]Universidade da Beira Interior, Calçada Fonte do Lameiro, 6201-001 Covilhã, Portugal

[b]Instituto Superior de Engenharia, Avenida Emídio Navarro, 1950-062 Lisboa, Portugal

[c]Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal

Publicado em: *Proceedings of the 3rd IASTED International Conference on Power and Energy Systems (EuroPES 2003), Marbella, Spain, September 3-5, 2003.*

In the electric liberalized energy framework, a utility with hydroelectric facilities faces the optimal trade-off problem of how to make the present profit by the management of the water resources without compromising future potential profit. This problem is known as the hydro scheduling problem. Hydro scheduling is a very important activity for hydroelectric power utilities because of its significant economic impact. This paper is on the problem of short-term hydro scheduling and the algorithmic aspects of its solution. Resources based on hydroelectric power producers with small storage capacities are known as run-of-the-river. Typically, run-of-the-river resources are considered to operate under stationary conditions at the maximum level of the reservoirs, corresponding by design to the optimum operating point. However, these stationary conditions are often not met, due to the head change effect. Because of the reservoirs low volume, the head may change and the operating efficiency becomes sensitive to the head. This non-linear effect coupled with the cascaded hydro configuration tends to give to this problem complexity and huge dimension. We propose a non-linear network mathematical programming approach to solve this problem, and we compare it with a linear network mathematical programming approach. Using numerical simulation results, we conclude that linear network mathematical programming is not suitable, thus non-linear network mathematical programming is more suitable.

VOLTAGE REGULATION SYSTEM DESIGN FOR THE FOUR-LEG CONVERTER

Vasco Soares[a,b], Pedro Verdelho[b]

[a]Departamento de Engenharia Electrotécnica e Automação, ISEL, Lisboa, Portugal

[b]Departamento de Engenharia Electrotécnica e de Computadores - Centro de Automática da Universidade Técnica de Lisboa, IST-CAUTL, Lisboa, Portugal

Publicado em: *10th European Conference on Power Electronics and Applications, Toulouse, França, Setembro de 2003*

Voltage regulation systems play an important role in all self powered systems connected to the ac mains, like active filters (AF's), unified power flow controllers (UPFC's), advanced static VAr compensators (ASVC's), PWM rectifiers, uninterruptible power supplies (UPS's) and neutral current compensators (NCC's). In some of these applications the voltage regulation is not the primary goal. However, voltage regulation is absolutely necessary to the operation of the voltage source converter (VSC) in order to sink or feed current into mains. When neutral current control is desirable, especially in active filtering with zero sequence current component compensation, three-phase four-wire converters are needed. They can be realized either with a four-leg VSC, as in the present study, or with a three-leg VSC with split dc link capacitor. Few works have been realized in the design of voltage regulators for these converters. Therefore, an insight study of the voltage regulation system design for the four leg converter is needed. This paper presents the voltage regulation system design for a three-phase four-wire voltage converter. The regulation system is applied to a four-leg voltage source converter connected to the ac mains. Dc voltage regulation system is analysed and the controller synthesis is realized. Digital simulation and experimental results with a DSP platform highlight the voltage regulation characteristics in terms of dynamic and steady state behaviour and also for robustness to disturbances influence.

PLANEAMENTO OPERACIONAL DE CURTO PRAZO PARA UMA CENTRAL HIDROELÉCTRICA

J.P.S. Catalão[a], S.J.P.S. Mariano[a], V.M.F. Mendes[b], L.A.F.M. Ferreira[c]

[a]Universidade da Beira Interior, Calçada Fonte do Lameiro, 6201-001 Covilhã, Portugal

[b]Instituto Superior de Engenharia, Avenida Emídio Navarro, 1950-062 Lisboa, Portugal

[c]Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal

Publicado em: *ENGENHARIA´2003-Inovação e Desenvolvimento,*
Covilhã, UBI, 5-7 de Novembro, 2003.

Esta comunicação endereça o problema de planeamento operacional de curto prazo para uma central hidroeléctrica, bem como os aspectos algorítmicos da sua solução. O tipo de recurso energético considerado exibe uma reduzida capacidade de armazenamento e é considerado a ”fio de água” para o planeamento. Tipicamente, considera-se que este recurso opera em condições estacionárias à cota máxima do reservatório que, em regra e por projecto, corresponde ao ponto de operação óptimo. Contudo, por razões de planeamento operacional, é muitas vezes desejável alterar esta política, incorrendo-se, por isso, em variações da altura de queda. Devido ao reduzido volume de água no reservatório, a altura de queda pode variar rapidamente e a eficiência de operação torna-se sensível à altura de queda – efeito de queda. Assim, a potência gerada é função não só do caudal turbinado mas também da altura de queda. Este efeito torna este problema não linear e de grande complexidade. Para a sua resolução é proposto um método de optimização baseado em programação não linear em rede, sendo comparado com o método, correntemente utilizado, baseado em programação linear em rede. Os resultados da simulação computacional mostram que a programação não linear em rede é o método de optimização mais apropriado.

SPECIAL PURPOSE ELECTRICAL MOTORS FOR EVS

José Carlos QUADRADO
Departamento de Engenharia Electrotécnica de Automação, ISEL, Lisboa, Portugal

Publicado em: *The 20th Internacional Electric Vehicle Symposium and Exposition, Long Beach,California, 15-19 November 2003*

In this paper the characteristics of an electric motor specially developed to be a prime mover of EVs are discussed. Being the main focus of this study the electrical motorized wheel, an overview of several proposed approaches is given.

Using as a starting point the necessary characteristics of the electrical motorized wheel, a special purpose electric motor was created that can be used as an motorized wheel for EVs in general. The major design characteristics of this special purpose electric motor are also presented in the current paper, including a possible mathematical model of the electrical motor.

The industrial applicability of the proposed motor is presented as well as the state of the art of the drive trains, proposed by several manufacturers that incorporate electrical motorized wheels, to characterize the current trends in the field.

EXCHANGE INTERACTION AND FERROMAGNETISM IN III-V SEMICONDUCTORS

[1,2]Dugaev VK, [3]Litvinov VI, [4]Barnas J, [1]Vieira M
[1] Department of Electronics and Communications, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emidio Navarro, 1949-014 Lisbon, Portugal
[2] Institute for Problems of Materials Science, Vilde 5, 58001 Chernovtsy, Ukraine
[3] WaveBand Corporation, 375 Van Ness Avenue, Suite 1105, Torrance, California 90501
[4] Department of Physics, Adam Mickiewicz University, ulica Umultowska 85, 61-614 Poznan´ , Polandand Institute of Molecular Physics, Polish Academy of Sciences, ulica M. Smoluchowskiego 17, 60-179 Poznan´ , Poland

Publicado em: *PHYSICAL REVIEW B67 (3): Art. No. 033201 JAN 15 2003*

The mechanism of indirect exchange interaction leading to ferromagnetism in magnetically doped III-V semiconductors is considered theoretically. The mechanism is based on the interplay of two interactions: (i) hybridization of band states with shallow impurity ones, and (ii) direct exchange coupling between localized spins and the band states. The indirect exchange interaction between two Mn impurities occurs when the wave functions of shallow states associated with the Mn atoms overlap. The mechanism does not rely on degenerate carriers, and therefore can describe the ferromagnetic transition in both degenerate and nondegenerate semiconductors. Ferromagnetic critical temperature has been calculated within the percolation approach, and is in good agreement with available experimental data.

NON PIXELLED AMORPHOUS SILICON BASED COLOR SENSORS.

M. Fernandes, Yu. Vygranenko, P. Louro, M. Vieira

Electronics Telecommunication and Computer Dept. ISEL, Rua Conselheiro Emídio Navarro, P 1949-014 Lisboa, Portugal

Publicado em: *Physics E. 16/3-4 (2003) pp.563-567.*

In recent works large area hydrogenated amorphous silicon p-i-n structures with low conductivity doped layers were proposed as single element image sensors. The working principle of this type of sensor is based on the modulation, by the local illumination conditions, of the photocurrent generated by a light beam scanning the active area of the device. In order to evaluate the sensor capabilities is necessary to perform a response time characterization. This work focuses on the transient response of such sensor and on the influence of the carbon contents of the doped layers. In order to evaluate the response time a set of devices with different percentage of carbon incorporation in the doped layers is analyzed by measuring the scanner-induced photocurrent under different bias conditions.

MECHANISM OF FERROMAGNETISM IN DILUTED MAGNETIC SEMICONDUCTORS AT LOW CARRIER DENSITY

[1,2]Dugaev VK, [3]Litvinov VI, [4]Barnas J, [3]Slobodskyy AH, Dobrowolski W, [1]Vieira M
1 Department of Electronics and Communications, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emidio Navarro, 1949-014 Lisbon, Portugal
2 Institute for Problems of Materials Science, Vilde 5, 58001 Chernovtsy, Ukraine
3 WaveBand Corporation, 375 Van Ness Avenue, Suite 1105, Torrance, California 90501
4 Department of Physics, Adam Mickiewicz University, ulica Umultowska 85, 61-614 Poznan´ , Polandand Institute of Molecular Physics, Polish Academy of Sciences, ulica M. Smoluchowskiego 17, 60-179 Poznan´ , Poland

Publicado em: *JOURNAL OF SUPERCONDUCTIVITY 16 (1): 67-70 FEB 2003*

We analyze critical temperature of ferromagnetic ordering in diluted magnetic semiconductors in the mean-field approximation. Using a general field-theoretical approach we formulate a description of magnetic phase transition, which takes into account the interaction of magnetic fluctuations. We also propose a mechanism of exchange interaction between Mn impurity moments in GaMnAs alloys via the Mn-induced acceptor levels. This mechanism may lead to low temperature ferromagnetism at vanishing concentration of free carriers.

MECHANISM OF FERROMAGNETISM IN DILUTED MAGNETIC SEMICONDUCTORS AT LOW CARRIER DENSITY

Dugaev VK, Litvinov VI, Barnas J, Slobodskyy AH, Dobr ,

Publicado em: 16 (1): 67-70, FEB 2003 PASPS

We analyze critical temperature of ferromagnetic ordering in diluted magnetic semiconductors in the mean-field approximation. Using a general field-theoretical approach we formulate a description of magnetic phase transition, which takes into account the interaction of magnetic fluctuations. We also propose a mechanism of exchange interaction between Mn impurity moments in GaMnAs alloys via the Mn-induced acceptor levels. This mechanism may lead to low temperature ferromagnetism at vanishing concentration of free carriers.

FERROMAGNETISM IN DILUTED MAGNETIC SEMICONDUCTORS AT LOW CARRIER DENSITY

[1,2]Dugaev VK, [3]Litvinov VI, [4]Barnas J, [3]Slobodskyy AH, [3]Dobrowolski W, [1]Vieira M
1 Department of Electronics and Communications, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emidio Navarro, 1949-014 Lisbon, Portugal
2 Institute for Problems of Materials Science, Vilde 5, 58001 Chernovtsy, Ukraine
3 WaveBand Corporation, 375 Van Ness Avenue, Suite 1105, Torrance, California 90501
4 Department of Physics, Adam Mickiewicz University, ulica Umultowska 85, 61-614 Poznan´ , Polandand Institute of Molecular Physics, Polish Academy of Sciences, ulica M. Smoluchowskiego 17, 60-179 Poznan´ , Poland

Publicado em: *PHYSICA STATUS SOLIDI B-BASIC RESEARCH, 236 (2): 507-510 MAR 2003*

We present a general approach to the problem of a ferromagnetic phase transition in diluted magnetic semiconductors with free carriers. The Curie temperature of ferromagnetic transition is calculated in the mean field approximation. The approach allows to analyze the effects of magnetic fluctuations and disorder on the Curie temperature. We also propose a new mechanism of exchange interaction between magnetic impurities at vanishing concentration of free carriers.

MODELING OF MAGNETICALLY CONTROLLED SI-BASED OPTOELECTRONIC DEVICES

[1,2]Dugaev VK, [1]Vygranenko Y, [1]Vieira M, [4]Litvinov VI, [3]Barnas
1 Department of Electronics and Communications, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emidio Navarro, 1949-014 Lisbon, Portugal
2 Institute for Problems of Materials Science, Vilde 5, 58001 Chernovtsy, Ukraine
3 WaveBand Corporation, 375 Van Ness Avenue, Suite 1105, Torrance, California 90501
4 Department of Physics, Adam Mickiewicz University, ulica Umultowska 85, 61-614 Poznan´ , Polandand Institute of Molecular Physics, Polish Academy of Sciences, ulica M. Smoluchowskiego 17, 60-179 Poznan´ , Poland

Publicado em: *PHYSICA E-LOW-DIMENSIONAL SYSTEMS & NANOSTRUCTURES 16 (3-4): 558-562 MAR 2003*

We present a theoretical analysis and results of modeling of a new integrated device for spintronics application, which is based on a hybrid metal-semiconductor structure. The proposed device consists of a Si-based p-i-n photodetector sandwiched between two layers of a ferromagnetic metal (3d ferromagnet or half-metallic compound). Electron-hole pairs are created in the semiconductor part of the structure by light illumination. The photocurrent flowing in such a system is shown to depend on its magnetic configuration. This is due to a difference in the specular reflection (as well as in the diffuse scattering) of spin-up and spin-down electrons and holes from magnetically polarized layers-similar to giant magnetoresistance effect in magnetic multilayers. This, in turn, allows controlling the device performance by an externally applied magnetic field. We have estimated magnitude of the effect and also determined the role of relevant material parameters.

OPTICAL PROPERTIES AND TRANSPORT IN PLD-GAN

[1]Niehus [1]M, Sanguino [4]P, Monteiro [4]T, Soares MJ, [4]Pereira E, [2]Vieira M, [3]Koynov S, [1]Schwarz R

[1] Inst Super Tecn, Dept Phys, Av Rovisco Pais 1, P-1096 Lisbon, Portugal
[2]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal;
[3] Bulgarian Acad Sci, CL SENES, Sofia 1784, Bulgária
[4]Univ Aveiro, Dept Phys, P-3810193 Aveiro, Portugal

Publicado em: *SOLID-STATE ELECTRONICS 47 (3): 569-573 MAR 2003*

We present structural, optical and transport data on GaN samples grown by hybrid, two-step low temperature pulsed laser deposition. The band gap of samples with good crystallinity has been deduced from optical spectra. Large below gap band tails were observed. In samples with the lowest crystalline quality the PL spectra are quite dependent on spot laser incidence. The most intense PL lines can be attributed to excitons bounded to stacking faults. When the crystalline quality of the samples is increased the ubiquitous yellow emission band can be detected following a quenching process described by a similar activation energy to that one found in MOCVD grown samples. The samples with the highest quality present, besides the yellow band, show a large near band edge emission which peaked at 3.47 eV and could be observed up to room temperature. The large width of the NBE is attributed to effect of a wide distribution of band tail states on the excitons. Photoconductivity data supports this interpretation. (C) 2002 Elsevier Science Ltd. All rights reserved.

BIAS CONTROLLED SPECTRAL SENSITIVITY IN A-SIC : H P-I-N DEVICES

Louro P, Vieira M, Fantoni A, Fernandes M, Vygranenko Y, Schwarz R

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal

Publicado em: *THIN SOLID FILMS 427 (1-2): 196-200, MAR 3 2003,*

Large area p-i-n amorphous silicon-carbon heterojunctions with low conductivity and wide band gap doped layers were produced by plasma enhanced chemical vapor deposition at low temperature. Carrier transport and collection efficiency are investigated from dark and illuminated current-voltage dependence and spectral response measurements under different electrical and optical bias conditions. The results show that it is possible to control the absorption at a given wavelength and thus to tune the spectral sensitivity by changing the electrical bias around the open circuit voltage. A numerical simulation gives insight into the physical process and explains the bias controlled spectral sensitivity presented by the devices.

FERROMAGNETISM IN DILUTED MAGNETIC SEMICONDUCTORS AT LOW CARRIER DENSITY

Dugaev VK, Litvinov VI, Barnas J, Slobodskyy AH, Dobrowolski W, Vieira M

Publicado em: *PHYSICA STATUS SOLIDI B-BASIC RESEARCH 236 (2): 507-510, MAR 2003*

We present a general approach to the problem of a ferromagnetic phase transition in diluted magnetic semiconductors with free carriers. The Curie temperature of ferromagnetic transition is calculated in the mean field approximation. The approach allows to analyze the effects of magnetic fluctuations and disorder on the Curie temperature. We also propose a new mechanism of exchange interaction between magnetic impurities at vanishing concentration of free carriers

MODELING OF MAGNETICALLY CONTROLLED SI-BASED OPTOELECTRONIC DEVICES

Dugaev VK, Vygranenko Y, Vieira M, Litvinov VI, Barnas J

Publicado em: *PHYSICA E-LOW-DIMENSIONAL SYSTEMS & NANOSTRUCTURES16 (3-4): 558-562, MAR 2003*

We present a theoretical analysis and results of modeling of a new integrated device for spintronics application, which is based on a hybrid metal-semiconductor structure. The proposed device consists of a Si-based p-i-n photodetector sandwiched between two layers of a ferromagnetic metal (3d ferromagnet or half-metallic compound). Electron-hole pairs are created in the semiconductor part of the structure by light illumination. The photocurrent flowing in such a system is shown to depend on its magnetic configuration. This is due to a difference in the specular reflection (as well as in the diffuse scattering) of spin-up and spin-down electrons and holes from magnetically polarized layers-similar to giant magnetoresistance effect in magnetic multilayers. This, in turn, allows controlling the device performance by an externally applied magnetic field. We have estimated magnitude of the effect and also determined the role of relevant material parameters. (C) 2002 Elsevier Science B.V. All rights reserved

OPTICAL PROPERTIES AND TRANSPORT IN PLD-GAN

Niehus M, Sanguino P, Monteiro T, Soares MJ, Pereira E, Vieira M, Koynov S, Schwarz R

Publicado em: *SOLID-STATE ELECTRONICS, 47 (3): 569-573, MAR 2003*

We present structural, optical and transport data on GaN samples grown by hybrid, two-step low temperature pulsed laser deposition. The band gap of samples with good crystallinity has been deduced from optical spectra. Large below gap band tails were observed. In samples with the lowest crystalline quality the PL spectra are quite dependent on spot laser incidence. The most intense PL lines can be attributed to excitons bounded to stacking faults. When the crystalline quality of the samples is increased the ubiquitous yellow emission band can be detected following a quenching process described by a similar activation energy to that one found in MOCVD grown samples. The samples with the highest quality present, besides the yellow band, show a large near band edge emission which peaked at 3.47 eV and could be observed up to room temperature. The large width of the NBE is attributed to effect of a wide distribution of band tail states on the excitons. Photoconductivity data supports this interpretation. (C) 2002 Elsevier Science Ltd. All rights reserved

HIGH SENSITIVE IMAGE SENSORS BASED ON A TANDEM LASER SCANNED PHOTODIODE

M. Vieira, M. Fernandes, P. Louro, A. Fantoni, I. Rodrigues

Electronics Telecommunication and Computer Dept. ISEL, Rua Conselheiro Emídio Navarro, P 1949-014 Lisboa, Portugal

Publicado em: *Proc. of II International Materials Symposium, (Lisbon, Portugal, April 14-16, 2003)*
Advanced Mateial Forum II, 91-95 (2003).

A new design based on a stacked n-i-p-n-i-p heterojunction is proposed for the Colour Laser Scanned Photodiode image sensor and compared with performance presented by a sensor whose capture element is based on a single p-i-n structure. Results show that the double structure presents a higher light-to-dark sensitivity. A black and white image is acquired with an improved resolution when compared with the single structure. The readout frequency is optimized showing that scans speeds up to 10^4 lines per second can be achieved without degradation in the resolution. A physical model is presented and supported by an electrical and a numerical simulation of the output characteristics of the sensor.

A-SIC:H TANDEM SOLAR CELLS: A NUMERICAL SIMULATION.

A. Fantoni [1,2,] P. Louro, I. Rodrigues[1], M. Fernandes[1], R. Schwarz[1], N. Carvalho[3] and M. Vieira[1]
[1] ISEL, Electronics Telecommunications and Computer Dept, R. Conselheiro Emidio Navarro, P 1949-014 Lisboa, Portugal
[2] CEMOP-UNINOVA, Campus da FCT-UNL, Quinta da Torre, 2825-Monte de Caparica, Portugal
[3] FCT-UNL, Dept. Ciência de Materiais, Campus da FCT-UNL, Quinta da Torre, 2825 Monte de Caparica, Portugal

Publicado em: *Proc. of II International Materials Symposium, (Lisbon, Portugal, April 14-16, 2003)*
Advanced Mateial Forum II, (2003).

Stacked a-Si:H pin/pin diodes are known to be more stable with respect to the light induced degradation than the conventional single junction pin structure. This can be ascribed to a better internal electric field distribution leading to an improved drift transport mechanism within the intrinsic layers. However the device performance can be limited by the reverted field associated with the internal n-p interface region (recombination junction). Such a different built-in field configuration leads to a device functioning fundamentally different from the standard p-i-n device, which can be well described through a detailed analysis of the internal electrical configuration of the device.

We present a study based on a numerical simulation about the behaviour of an a-SiC:H pin/ a-Si:H pin monolithic tandem solar cell and we compare them with the characteristics of a tandem solar cell with the same characteristics produced by rf PE-CVD. Junction properties, carrier transport, photogeneration and collection efficiency are investigated from dark and illuminated current-voltage characteristics and spectral response measurements, with and without additional background illumination and under different light bias conditions.

STACKED A-SIC:H OPTICAL TRANSDUCERS: THE INFLUENCE OF THE SENSING MATERIAL

P. Louro, M. Fernandes, I. Rodrigues, A. Fantoni, and M. Vieira, Electronics
Telecommunications and Computer Dept., ISEL, R. Conselheiro Emidio Navarro, P 1949-014 Lisboa,
Portugal. Tel: +351 21 8317290, Fax: +351 21 8317114, e-mail: plouro@isel.pt

Publicado em: *Proc. of II International Materials Symposium, (Lisbon, Portugal, April 14-16, 2003)*
Advanced Mateial Forum II, 81-85, 2003.

The efforts are focused mainly on doped n- and p-type layers at high and low doping levels with and without carbon, as well as in the intrinsic layer thickness and composition. The structural and optoelectronic properties of the single layers were determined through infrared and visible spectroscopy, temperature-dependent conductivity, and were complemented by CPM measurements. Junction properties, carrier transport, photogeneration and collection efficiency are investigated from dark and illuminated current-voltage characteristics and spectral response measurements, with and without additional background illumination and under different light bias conditions.

Results show that the collection efficiency depends strongly on the structure of the device (single or stacked).

The obtained results show that an accurate engineering of the interfaces, in terms of optical gap and band-bending control can improve collection efficiency, showing that the interface band banding can be managed to create a monolithic tandem solar cell working almost as two cells connected in series. The importance of a well balanced photogeneration between the two sub-cells has also been outlined, aiming to indicate the need to determine an optimal configuration of the absorber layers (in terms of optical gap and thickness) so advantage can be taken of local fields created by band discontinuities at the internal n/p interface.

STACKED PIN-PIN HETEROJUNCTIONS FOR IMAGE RECOGNITION AND COULOR SEPARATION

M. VIEIRA, P. LOURO, A. FANTONI, M. FERNANDES, D. BRIDA, M. VIEIRA,

M. Electronics Telecommunications and Computer Dept, ISEL, Lisbon, Portugal, Yu. Vygranenko, Univ. Waterloo, Canada.

Publicado em: *Amorphous and heterogeneous silicon based films-2002, (S. Francisco, April 21-25 USA), Mat. Res. Soc. Symp. Proc 762@2003 A.18.13.1*

A new design based on a stacked n-i-p-n-i-p structure is proposed for the Colour Laser Scanned Photodiode sensor, CLSP. The CLSP is a two terminal sensor based on one single large area p-i-n sensing element and a scanning reader. In short circuit mode, it can detect a black and white image. Under forward bias, colour separation is possible, with a reasonable rejection rate. No optical filters are used during the image acquisition process.

To tune the spectral sensitivity of the device we propose a stacked metal/nipnip/metal sensing element. The first p-i-n photodiode confines the carriers at the illuminated regions while the second one, driven by the scanner, gives information on their location (image shape) density (image intensity) and absorbed wavelength (image colour). In this work the efforts are focused mainly on the design of the structure and composition of the layers and its role on sensor performance.

STACKED N-I-P-N-I-P HETEROJUNCTIONS FOR IMAGE RECOGNITION

Vieira M, Fantoni A, Fernandes M, Louro P, Rodrigues I.

Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal

Publicado em: *AMORPHOUS AND NANOCRYSTALLINE SILICON-BASED FILMS-2003 Editors: Abelson JR, Ganguly G, Matsumura H, Robertson J, Schiff EA MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS, 762199-204, 2003*

This work aims to clarify possible improvements and physical limits of the Color Laser Scanned Photodiode image sensor when used as high sensitive non-pixel image reader. A new design based on a stacked n-i-p-n-i-p heterojunction is proposed and compared with the old single n-i-p sensing structure. Results show that a B-W image is acquired with an improved resolution. The readout frequency is optimized showing that scans speeds up to 10(4) lines per second can be achieved without degradation in the resolution. A physical model is presented and supported by an electrical and a numerical simulation of the output characteristics of the sensor.

An Open Integration Bus for EFC: the ITS-IBUS

J. Sales Gomes[1], Gastão Jacquet[1], Miguel Machado[1], A. Luís Osório[2],
Carlos Gonçalves[2], Manuel Barata[2]

[1] BRISA, Auto-estradas de Portugal, DID Innovation and Development Department, Carcavelos, Portugal;

[2] ISEL, Instituto Superior de Engenharia de Lisboa, DEETC department, Lisboa, Portugal

Publicado em: Actas da conferência ASECAP-2003, 18 - 21 de Maio de 2003 em Portoroz, Slovenia

The project BRISA ITS-IBus (Intelligent Transport Systems Integration Bus) aims at developing the architecture for a technological platform and business process modeling tools, able to establish a uniform integration framework to toll related system. A general purpose electronic fee collection process requires the support from different technological systems, in most cases integrated one by one on a bilateral agreement basis. The growing flexibility required from the toll infrastructures to support new business models and the need to reduce development and management costs are motivating an extra effort from different players to promote standards or, at least, opened and widely accepted consensus. The CEN initiative to normalize DSRC (Dedicated Short Range Communications) under TC-278 is an example of such an effort to promote interoperability and cost reduction by increasing reutilization.

A-SIC:H TANDEM SOLAR CELLS: CHARACTERIZATION AND NUMERICAL SIMULATION

A. Fantoni[1,2,] M. Fernandes[1], P. Louro[1], M. [Vieira1]
[1] ISEL-DEETC, Rua Conselheiro Emidio Navarro, 1949-014 Lisboa, Portugal
[2] FCT-UNL, 2825 Monte de Caparica, Portugal

Publicado em: *Proc. of European Materials Research Society Symposium, (Strasburg, France, 10-13, June, 2003) Sensor and Actuators (in press).*

Stacked a-Si:H p-i-n/p-i-n diodes are known to be more stable with respect to the light induced degradation than the conventional single junction p-i-n structure. We present a study, based on a numerical simulation, about the internal behavior of an a-SiC:H pin/ a-Si:H pin monolithic tandem solar cell. The results we show that an accurate engineering of the internal n/p interface, in terms of optical gap and band banding control can improve the solar cell efficiency, showing that the interface band bending can be managed to create a monolithic tandem solar cell working almost as two cell connected in series. The importance of a well balanced photogeneration between the two sub-cells has been also outlined, aiming to indicate the need to determine an optimal configuration of the absorber layers (optical gap and thickness) in order to take profit from the local fields created by the band discontinuities at the internal n/p interface.

LARGE AREA IMAGE SENSING STRUCTURES BASED ON A-SIC:H : A DYNAMIC CHARACTERIZATION

M. FERNANDES(1), M. VIEIRA(1) I. RODRIGUES(1) AND R. MARTINS(2)

(1)ISEL, Electronics Telecommunications and Computer Dept., R. Conselheiro Emídio Navarro, P 1949-014 Lisboa, Portugal

(2)FCT-UNL Materials Science Dept, Campus da FCT-UNL, Quinta da torre, 2825 Monte da Caparica, Portugal.

Publicado em: *Proc. of European Materials Research Society Symposium, (Strasburg, France, 10-13, June, 2003) Sensor and Actuators (in press).*

In recent works large area hydrogenated amorphous silicon p-i-n structures with low conductivity doped layers were proposed as single element image sensors. The working principle of this type of sensor is based on the modulation, by the local illumination conditions, of the photocurrent generated by a light beam scanning the active area of the device. In order to evaluate the sensor capabilities is necessary to perform a response time characterization. This work focuses on the transient response of such sensor and on the influence of the carbon contents of the doped layers. In order to evaluate the response time a set of devices with different percentage of carbon incorporation in the doped layers is analyzed by measuring the scanner-induced photocurrent under different bias conditions.

OPTICAL CONFINEMENT AND COLOUR SEPARATION IN A DOUBLE COLOUR LASER SCANNED PHOTODIODE (D/CLSP)

M. VIEIRA, M. FERNANDES, P. LOURO, A. FANTONI, I. RODRIGUES
Electronics Telecommunication and Computer Dept. ISEL, Rua Conselheiro Emídio Navarro, P 1949-014 Lisboa, Portugal

Publicado em: *Proc. Transducers 2003, (Boston Massachussetts, USA, 8-12, June, 2003). Sensor and Actuators (in press).*

Large area n-i-p-n-i-p a-SiC:H heterostructures are used as sensing element in a Double Color Laser Scanned Photodiode image sensor (D/CLSP).

This work aims to clarify possible improvements, physical limits and performance of CLSP image sensor when used as non-pixel image reader. Here, the image capture device and the scanning reader are optimized and the effects of the sensor structure on the output characteristics discussed.

The role of the design of the sensing element, the doped layer composition and thickness, the read-out parameters (applied voltage and scanner frequency) on the image acquisition and the color detection process are analyzed.

A physical model is presented and supported by a numerical simulation of the output characteristics of the sensor.

INTERNAL ION MOLECULE REACTIONS INSIDE HETEROGENEOUS CLUSTERS TRIGGERED BY PHOTON IMPACT”

J. M. A. Frazão[1], J. C. A. Trindade, J. M. C. Lourenço[2], M. Áurea Cunha[3], M. L. Bhatt and A. M. C. Moutinho [2]

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal E-mail:frazao@popsrv.ist.utl.pt; [2]CeFITec, Departamento de Física, Faculdade de Ciências e Tecnologia ,UNL, [3] Departamento de Física, Instituto Superior Técnico, UTL.

Publicado em: *Book of Abstracts, XX International Symposium on Molecular Beams, Lisboa 8-13 Junho de 2003*

It is well know that molecular clusters are suitable systems to study elementary molecular reacting processes between a small and a controlled number of molecular species in presence.

In previous studies we have reported different mechanisms involved in internal clusters ion molecular reactions (ICIMR) triggered when molecular clusters are ionized by electron impact. In the present work we intend to continue and compare the study of these reactions replacing the electron impact ionization of the neutral clusters by a multiphoton ionization process.

Heterogeneous CO_2 and OCS clusters are obtained by isentropic expansions of these gases seeded in argon. The ICIMR reactions taking place inside these clusters after multiphoton ionization will be presented.

This work is part of the project POCTI/33244/FIS/2000 of the Fundação para a Ciência e a Tecnologia, Portugal.

EXTENDING BDI WITH EMOTIONAL DISPOSITIONS FOR ADAPTIVE SOCIAL REASONING

Luís Morgado[1], Graça Gaspar[2]

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores, ISEL, Lisboa, Portugal, E-mail: lm@isel.ipl.pt;

[2]Faculdade de Ciências da Universidade de Lisboa, Portugal,
E-mail: gg@di.fc.ul.pt

Publicado em: *Proceedings of the 2nd International Workshop on Regulated Agent-Based Social Systems: Theories and Applications (RASTA'03).*

In dynamic and uncertain environments, where agents can have different behavior profiles, the ability to reason about the other agents in order to coordinate their activities raises many problems. In this paper we argue that adaptive motivational mechanisms are fundamental to address these problems, and that emotion can be a key element in the definition of those mechanisms. In this line of thought, we present an agent model of emotional disposition and show how it could be used to extend a classical BDI model for adaptive behavior, in a context of social interaction.

EMOTION IN INTELLIGENT VIRTUAL AGENTS: THE FLOW MODEL OF EMOTION

Luís Morgado[1], *Graça Gaspar*[2]

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores, ISEL, Lisboa, Portugal, E-mail: lm@isel.ipl.pt; [2]Faculdade de Ciências da Universidade de Lisboa, Portugal,
E-mail: gg@di.fc.ul.pt

Publicado em: *Rist, T. et al (Eds), Intelligent Virtual Agents, Proc. of IVA 2003, LNAI 2792, Springer-Verlag, 2003.*

Different models have been proposed to support emotion in artificial agents. However, a general framework to support the implementation of emotional agents of different kinds and levels of complexity is still not well defined. In this paper we present a model that is independent of specific physiological or psychological details, despite being inspired by biological processes, defining an emotional structure that can be objectively implemented and evaluated, and which can be used to integrate and extend other agent models, like deliberative models. Concrete results are presented to illustrate the model adequacy for agent emotional characterization.

OPTIMISATION OF CELL RADIUS IN UMTS-FDD NETWORKS

António Serrador[1] e Luís M. Correia[2]

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal E-mail:aserrador@deetc.isel.ipl.pt; [2]Instituto de Telecomunicações –IST, Lisboa, Portugal E-mail: luis.correia@lx.it.pt

Publicado em: in *Proc. of MWCS'03 12 th IST Mobile & Wireless Communications Summit, Aveiro, Portugal, June 2003*

This work is focus on a key subject for Third Generation (3G) mobile operators, which is planning and optimising a UMTS-FDD multi-service mobile radio network. A planning and optimisation tool is presented, which optimises the cell radius as a function of a given scenario, users services characterisation, general radio network aspects, and quality indicators. Using this tool, impact and tendencies of several parameters over optimum cell radius are analysed, like urban characterisation parameters, population density, and general system configurations. Basically, linear and quadratic trends are obtained. For example, the population density impact on the cell radius, ranging from 2 500 to 20 000 persons/km^2 (only voice active), results in a cell radius from 700 to 400 m, respectively.

TRACKING GROUPS OF PEDESTRIANS IN VIDEO SEQUENCES

Jorge S. Marques[1], Pedro M. Jorge[2], Arnaldo J. Abrantes[3] e J. M. Lemos[4]
[1]IST/Instituto de Sistemas e Robótica (ISR), [2]ISEL/ISR; [3]ISEL, [4]INESC-ID/IST

Publicado em*:* *2003 IEEE Workshop on Multi-object Tracking (WOMOT), Madison USA, June 2003.*

This paper describes an algorithm for tracking groups of objects in video sequences. The main difficulties addressed in this work concern total occlusions of the objects to be tracked as well as group merging and splitting. A two layer solution is proposed to overcome these difficulties. The first layer produces a set of spatio temporal strokes based on low level operations which manage to track the active regions most of the time. The second layer performs a consistent labeling of the detected segments using a statistical model based on Bayesian networks. The Bayesian network is recursively computed during the tracking operation and allows the update of the tracker results everytime new information

is available. Experimental tests are included to show the performance of the algorithm in ambiguous situations.

I-Q MONOLITHIC OSCILLATOR DESIGN ON STANDARD CMOS TECHNOLOGY

Fernando Fortes, Fernando Azevedo, Maria João do Rosário

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal E-mail: ffortes@deetc.isel.ipl.pt.; [2]Istituto de Telecomunicações; [3]Instituto Superior Técnico

Publicado em: *ConfTele2003, 4th Conference on Telecommunications, Aveiro, Portugal*

This paper describes the design of an RC monolithic oscillator with quadrature outputs. Insight is given on a quadrature oscillator concept, followed by the adequate circuit topology for standard CMOS implementation. Presented simulations show the CMOS circuit ability to implement this kind of oscillators at high frequencies.

The layout is also presented, with proper design for 900MHz operation. It shows a compact design with a total area of 0.2mm2.

A 1.9GHz CMOS MONOLITHIC UP-CONVERTION MIXER

Fernando Azevedo[1,2], Fernando Fortes[1,2], Maria João Rosário[2,3]

[1]Departamento de Engenharia de Electrónica e Telecomunicações, ISEL, Lisboa, Portugal, [2]Instituto de Telecomunicações, Lisboa, Portugal, [3]Instituto Superior Técnico, Lisboa, Portugal.

Publicado em: *ConfTele2003 - IVth Tele-communications Conference, Vol.1 pp.83-86, 18-20 June 2003, Aveiro, Portugal.*

Wireless communications technology has been one of the fastest growing technologies during the last years. The new opportunities created with this advent allows the development of more innovative, low-cost, low power and robust solutions emphasizing higher integration and less weight.

Actually CMOS is the best solution process for low cost and high integration. The development of high performance RF front-ends requires innovative RF circuit designs to make the best of a good technology and reduce the off-chip discrete components. To reduce the off-chip components the mixer is a very important key-part in transceiver design. Mixers are found in all wireless communications systems and, as the level integration is increased and passive off-chip elements in RFIC are eliminated, conversion gain and port-to-port isolation will be required to compensate the lower LO and the reduced performance filtering on-chip.

This paper describes the design and simulation of a 1.9GHz monolithic Up-Converter mixer implemented in a standard 0,6μm CMOS technology. The simulations were performed with BSIM3 model. The mixer presents 15dB conversion gain at 1.9GHz for 3.3V power supply with a LO drive of 1dBm while consuming 2mA. The third-order input intercept point is +6dBm and the input 1dB compression point is -4dBm. The mixer employs an all n-channel devices and resistive loads for high frequency operation and requires no inductors on or off-chip. As all the devices are fabricated on a single chip, the balance is very good and high spurious rejection is obtained.

CAPACITY OF MIMO SYSTEMS BASED ON COST 259 DCM SIMULATIONS

[1,2]Pedro Vieira, [2]António Rodrigues

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal; [2]Instituto das Telecomunicações (IT) / Instituto Superior Técnico

Publicado em: *Proceedings of 4th Conference on Telecommunications, Aveiro, Portugal, Junho de 2003, pp. 9-12.*

Capacity of MIMO (multiple-input/multiple-output) Systems based on COST 259 channel model simulations are presented in this paper, for two different radio environments, micro- and picocell.

Two different power allocation strategies are considered, “water filling” and uniform and two different antenna topologies, 4x4 and 2x4.

It is shown that space diversity used at the MIMO radio link is an efficient technique mainly in the picocell scenario, achieving capacities of 17 bit/s/Hz for 50% outage level using a 4x4 antenna configuration implementing water-filling at a SNR of 20 dB.

PHOTOCURRENT PROFILE IN A-SI:H TANDEM STRUCTURES: DEPENDENCE ON THE ILLUMINATION CONDITIONS.

A. FANTONI, M.FERNANDES, P.LOURO, I.RODRIGUES, M.VIEIRA
ISEL, Electronics Telecommunications and Computer Department., R. Conselheiro Emidio Navarro, 1949-014 Lisboa, Portugal.

Publicado em: *Proc. of International conference on amorphous and microcrystalline semiconductors: Science and Technology, (Campos do Jordão SP, Brazil, August 25-29, 2003*

We present in this paper results about the analysis of the photocurrent in a-Si:H tandem structures. It is well known in literature that, in order to optimize the light power conversion, the geometry of the cell and the thickness of the absorber layers must be adjusted to the light absorption profile. If there is a mismatch between the number of the electron-hole pairs generated in the sub-cells, the total collected current is limited by the sub-cell absorbing the lowest number of photons. We have found the photocurrent profile in these conditions to be dependent on the light absorption profile, that is, on the incident light wavelength and intensity. Our experiments and analysis reveal the photocurrent profile to have a strong nonlinear dependence on the externally applied bias in the range around to the open circuit value, indicating the superposition of different, concurring effects that lead the photocurrent to alternatively increase and decrease before finally entering in its secondary state.

Our interpretation point out the cause of such effect to a self biasing of the bottom cell under certain unbalanced light generation of carriers and an asymmetric reaction of the internal electric fields to the externally imposed forward bias.

OPTICALLY ADDRESSED READ-WRITE DEVICE BASED ON A TANDEM HETEROSTRUCTURES

M. VIEIRA, M. FERNANDES, A. FANTONI, P. LOURO, AND R. SCHWARZ
[1]Electronics Telecommunications and Computer Dept., ISEL, R. Conselheiro Emídio Navarro, P 1949-014 Lisboa, Portugal.

Publicado em: *Proc. of International conference on amorphous and microcrystalline semiconductors: Science and Technology, (Campos do Jordão SP, Brazil, August 25-29, 2003).J. Non Cryst. Solids (in press)*

An optically addressed read-write sensor based on two stacked p-i-n heterojunctions is analyzed. The device is a two terminal image sensing structure. The charge packets are injected optically into the p-i-n writer and confined at the illuminated regions changing locally the electrical field profile across the p-i-n reader. An optical scanner is used for charge readout.

The role of the sensor configuration and readout parameters on the image acquisition process is analyzed. The presence of a metallic light-screening layer between the writer and the reader proved to be effective to optically decouple the two p-i-n structures, while maintaining good electrical conductivity. The optical-to-electrical transfer characteristics show high quantum efficiency, broad spectral response, and reciprocity between light and image signal. A numerical simulation supports the imaging process.

OPTOELECTRONIC CHARACTERIZATION OF A-SIC:H STACKED DEVICES

P. LOURO, A. FANTONI, M. FERNANDES, A. MAÇARICO, R. SCHWARZ AND M. VIEIRA
ISEL, Electronics Telecommunications and Computer Dept, R. Conselheiro Emidio Navarro, P 1949-014 Lisboa, Portugal,.

Publicado em: *Proc. of International conference on amorphous and microcrystalline semiconductors: Science and Technology, (Campos do Jordão SP, Brazil, August 25-29, 2003).J. Non Cryst. Solids (in press)*

The aim of this work is the optoelectronic characterization of double p-i-n stacked devices based on a-Si alloys materials, in order to evaluate their suitability in large area optical sensors.

Photogeneration, collection efficiency and carrier transport are investigated from dark and illuminated current-voltage characteristics and spectral response measurements, with and without additional background illumination and different electrical bias conditions.

Results show that the collection efficiency depends on the device configuration and on the optical and electrical bias. The carrier collection is mainly dependent on the front and back intrinsic layers thickness and on the composition of the p-type doped layers. When wide band gap p-layers are used, the asymmetric distribution of the electrical field controls the transport mechanism. Under red optical bias the electrical field is enhanced at the front cell and decreased at the back one leading to an increased red light-to dark sensitivity.

A numerical simulation supports the discussion of the experimental results. Considerations about induced electric field and inversion layers at the interfaces and generation-recombination process are used to explain the devices output.

A GEOMETRIC APPROACH TO MOTION TRACKING IN MANIFOLDS

J. G. Silva[1], J. S. Marques[2], J. M. Lemos[3]

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal E-mail: jgs@isel.ipl.pt; [2]IST/ISR, Lisboa, Portugal E-mail: jsm@isr.ist.utl.pt; [3]INESC-ID/IST, Lisboa, Portugal E-mail: jlml@inesc.pt

Publicado em: *13th IFAC Symposium on System Identification, Rotterdam, The Netherlands, August 2003*

In many multi-dimensional tracking problems, the quantities of interest are restricted to a manifold in observation space. Learning the manifold shape is a necessary step for dimensionality reduction, which in turn allows faster and more robust tracking performance. For manifolds with arbitrary topology, learning the shape from noisy scattered data is not trivial. This paper presents a geometric approach that is valid for arbitrary manifold dimension and topology. An approximation of the tangent bundle is computed by region growing, making it possible to estimate a set of manifold charts. A tracking algorithm which takes advantage of the geometric information thus found is also presented.

NOVEL STRUCTURE FOR LARGE AREA IMAGE SENSING

M. FERNANDES[1], M. VIEIRA[1] AND R. MARTINS[2]
[1] ISEL, Electronics and Communications Dept., R. Cons. Emídio Navarro, 1949-014 Lisboa, Portugal
[2] FCTUNL, Materials Sc. Dept, Portugal

Publicado em: *Proc. 17th European Conference on Solid-State Transducers "Eurosensors XVII", Guimaraes, Portugal, September 21 –Sensor and Actuators (in press).*

This work presents preliminary results in the study of a novel structure for a Laser Scanned Photodiode (LSP) type of image sensor. In order to increase the signal output, a stacked n-i-p-n-i-p structure with an intermediate light blocking layer. The image and scanner are absorbed in separated junctions; the device photocurrent is dependent on the local illumination conditions on the image side junction. The results show that the structure can be successfully used as an image sensor even though some optimization is needed to enhance the performance of the device.

A NON-PIXEL IMAGE READER FOR CONTINUOUS IMAGE DETECTION BASED ON TANDEM HETEROSTRUCTURES

M. VIEIRA, M. FERNANDES, P. LOURO, A. FANTONI AND I. RODRIGUES

Electronics Telecommunications and Computer Dept., ISEL, R. Conselheiro Emídio Navarro 1, 1900-014 Lisbon, Portugal

Publicado em: *Proc. 17th European Conference on Solid-State Transducers "Eurosensors XVII", Guimaraes, Portugal, September 21 –Sensor and Actuators (in press).*

Large area stacked n-i-p(a-Si:H)/n-i-p(a-SiC:H) heterostructures are used as Colour Laser Scanned Photodiode image sensors. The sensor consists on one large cell sensing element and an optical scanner. The design allows a continuous readout without the need for pixel-level patterning. The role of light pattern and scanner wavelengths on the readout parameters is analyzed. To avoid image smearing, a significant improvement is achieved by confining the carriers generated by the light pattern at the back photodetector and the ones generated by the scanner at front reader. Results show that the highest resolution and contrast is achieved with a green light pattern and a blue scanner. A black and white image is acquired with a resolution around 20 μm showing the potentiality of these devices for imaging applications. The readout frequency is optimized showing that the scan speed can go up to 104 lines per second without degradation in the resolution. Electrical and numerical simulations support the results.

FAST ACQUISITION AND TRACKING IN GNSS RECEIVERS AN INNOVATIONS-BASED APPROACH

Fernando M. G. Sousa[a]; José M. N. Leitão[b]

[a]Instituto Superior de Engenharia de Lisboa; [b]Instituto Superior Técnico.

Publicado em: *Proceedings of the SPC2003 – ESA, Eight International Workshop on Signal Processing Techniques for Space Communications, pp. 412-419, Catania, Italy, September, 2003.*

Global navigation satellite system (GNSS) receivers perform a two-dimensional search to acquire code phase and Doppler shift information. In the conventional architectures, the Doppler frequency is estimated at different resolutions at different stages of the acquisition algorithm to pull-in track. Tracking is performed with two loops: one to track the code and the other one to track the carrier frequency. Instead the multi-stage frequency search, in this paper we propose a new open-loop technique using a bank of stochastic nonlinear filters (NLF). After coarse acquisition, the bank of NLF performs fine acquisition and tracking of phase and Doppler. Simulation results show the relevance of the adopted approach.

CLASS ADAPTED IMAGE COMPRESSION USING INDEPENDENT COMPONENT ANALYSIS

Artur J. Ferreira[1] e Mário A. T. Figueiredo[2]

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal E-mail: arturj@cc.isel.ipl.pt ; [2]Departamento de Engenharia Electrotécnica e de Computadores, IST, Lisboa, Portugal E-mail: mtf@lx.it.pt

Publicado em: *ICIP03-IEEE International Conference on Image Processing, vol. 1, pp. 625-629, Barcelona, Espanha, Setembro 2003*

This paper exploits *independent component analysis* (ICA) to obtain transform-based compression schemes adapted to specific image classes. This adaptation results from the data-dependent nature of the ICA bases, learnt from training images. Several coder architectures are evaluated and compared, according to both standard (SNR) and perceptual (*picture quality scale* – PQS) criteria, on two classes of images: faces and fingerprints. For fingerprint images, our coders perform close to the well-known special-purpose wavelet-based coder developed by the FBI. For face images, our ICA-based coders clearly outperform JPEG at the low bit-rates herein considered.

IMAGE COMPRESSION USING ORTHOGONALIZED INDEPENDENT COMPONENTS BASES

Artur J. Ferreira[1] e Mário A. T. Figueiredo[2]

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal E-mail: arturj@cc.isel.ipl.pt ; [2]Departamento de Engenharia Electrotécnica e de Computadores, IST, Lisboa, Portugal E-mail: mtf@lx.it.pt

Publicado em: *NNSP'03-IEEE Neural Networks for Signal Processing, pp. 689-699, Toulouse, França, Setembro 2003.*

In this paper we address the orthogonalization of *independent component analysis* (ICA) to obtain transform-based image coders. We consider several classes of training images, from which we extract the independent components, followed by orthogonalization, obtaining bases for image coding.

Experimental tests show the generalization ability of ICA of natural images, and the adaptation ability to specific classes.

The proposed fixed size block coders have lower transform complexity than JPEG. They outperform JPEG, on several classes of images, for a given range of compression ratios, according to both standard (SNR) and perceptual (picture quality scale - PQS) measures. For some image classes, the visual quality of the images obtained with our coders is similar to that obtained by JPEG2000, which is currently the state of the art still image coder. On fingerprint images, our fixed and variable size block coders perform competitively with the special-purpose wavelet-based coder developed by the FBI.

UNDERLYING ITS BUSINESS PROCESSES WITH FLEXIBLE AND PLUGGED PEER SYSTEMS:THE OPEN ITS-IBUS APPROACH

A. Luís Osório[1], M. Martins Barata[1], Arnaldo J. Abrantes[1],J. Sales Gomes[2], Gastão C. Jacquet[2]

[1] ISEL, Instituto Superior de Engenharia de Lisboa, DEETC department, Lisboa, Portugal;

[2] BRISA, Auto-estradas de Portugal, DID Innovation and Development Department, Carcavelos, Portugal

Publicado em: *“Processes and Foundations for Virtual Organizations”, Kluwer Academic Publishers, ISBN: 1-4020-7638-X, pages 221-230, em 2003*

The extension of the Via-Verde business model from motorways and bridges to car parking and gas stations involving different enterprises has motivated the proposal of an open integration bus to answer the new challenges for systems integration. It is discussed a service framework based on a peer to peer distributed architecture where peers offer specialized services contributing to the execution of virtual business processes. Those specialized services are executed in a system container with “plug and play” features and some of them assume the responsibility for the execution and coordination of the business processes. The paper discusses the underlying strategy that has motivated BRISA, as ITS end-user, to promote an open strategy for the ITS-IBus integration framework. It is also discussed a strategy based on a distributed service framework offering an added flexibility to virtual business process execution and coordination.

FLEXIBLE AND PLUGGED PEER SYSTEMS INTEGRATION TO ITS-IBUS: THE CASE OF EFC AND LPR SYSTEMS

A. Luís Osório[1], Arnaldo J. Abrantes[1], Jorge C. Gonçalves[1], Paulo Araújo[1], J. Miguel Machado[2], Gastão C. Jacquet[2], J. Sales Gomes[2]

[1] ISEL, Instituto Superior de Engenharia de Lisboa, DEETC department, Lisboa, Portugal;

[2] BRISA, Auto-estradas de Portugal, DID Innovation and Development Department, Carcavelos, Portugal

Publicado em: *Processes and Foundations for Virtual Organizations”, Kluwer Academic Publishers, ISBN: 1-4020-7638-X, pages 231-240, em 2003*

The development of new services to motorway users extending electronic fee collection (EFC) to car parking and gas stations requires an added flexibility from the underlying technological framework. The implementation of these facilities requires a new flexibility from the technological framework able to cope with the complex distributed cooperative processes crossing different companies. This paper describes the strategy adopted by the ITS-IBus project to promote a new organization for the toll underlying technologies, able to create the conditions to challenge new, flexible and innovative services. The adoption of a service based framework associated to the definition of a set of open interfaces based on existing standards is discussed.

CMOS MONOLITHIC WIDEBAND IMAGE REJECTION MIXER WITH POLYPHASE FILTERS

Fernando Azevedo[1,3], Maria João Rosário[2,3], João Costa Freire[2,3]

[1]Departamento de Engenharia de Electrónica e Telecomunicações, ISEL, Lisboa, Portugal, [2]Instituto Superior Técnico, Lisboa, Portugal, [3]Instituto de Telecomunicações, Lisboa, Portugal.

Publicado em: *IMOC-International Microwave and Optoelectrónics Conference, Vol.2 pp.815-818, 20-23 September 2003, Foz do Iguaçu, Brazil.*

Image rejection ratio in double balanced mixers is strongly dependent on the balance between its branches. The influence of mismatches is analysed and conclusions on the key aspects of the design to increase the image rejection are discussed. A practical circuit implementation is described: a 1.9GHz downconversion image rejection mixer is fabricated in 0.6μm CMOS standard technology. Measurements on the prototype showed a 34dB image rejection and an overall conversion gain of 16dB.

The growing needs for low power, low cost and highly integrated wireless mobile transceivers, have motivated researchers to present new monolithic solutions implemented in standard CMOS technology. One very important key-part of transceiver design that allows eliminating off-chip discrete components, for fully integration, is the mixer. The wide-band intermediate frequency (IF) architecture converts all radio frequency (RF) spectrum, passing through the input RF filter, directly to base band (BB) as in the case of direct conversion receivers. No band pass filtering is performed at IF. However, differently to direct conversion, the translation takes place in two steps, using two local oscillators (LO) and two sets of mixers. This provides the following main advantages: no oscillator operates at RF input frequency; tuning the receiver can be accomplished with the second LO at a lower frequency.

The double balanced mixer presented is an image rejection (IR) converter that uses six balanced mixers to implement the above referred architecture. Each balanced mixer can be easily implemented with CMOS Gilbert cells. If the branches are perfectly matched and the local oscillators are applied in quadrature the image ($IM-f_{IM}=2f_{LO}-f_{RF}$) is fully rejected.

MULTI SERVICE CELL LOAD ESTIMATION ON UMTS-FDD

Autores António Serrador[1] e Luís M. Correia[2]

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal E-mail:aserrador@deetc.isel.ipl.pt; [2]Instituto de Telecomunicações –IST, Lisboa, Portugal E-mail: luis.correia@lx.it.pt

Publicado em: in *Proc. of WPMC'03 - 6 th International Symposium on Wireless Personal Multimedia Communications*, Yokosuka, Kanagawa, *Japão, Outubro 2003.*

This work is focused on a key subject for third generation mobile operators, which is planning the UMTS-FDD multi-service network In order to achieve this goal, a UMTS system level simulator was built accounting for coverage and traffic, and implementing system load calculation algorithms. This simulator implements some of the most representative ("killer applications") services, based on their respective source model at circuit or packet switch level, being mapped onto the FDD radio interface. The following traffic source models were implemented: Voice, e-mail and FTP, SMS, MMS, WWW, LBS and Streaming, and Video; most of the models are packet oriented, as the one presented by ETSI and the ON/OFF time and volume based model. Circuit and packet switch based services are distinguished as well by their real and non-real time dependence. The multiple services integration on a simulator allows a better and more accurate network performance analysis. A micro-cell propagation model, link budget, antenna pattern, channel codes and power constrains were also incorporated. Using this tool, the impact of several parameters over the cell load is analysed. For example running all services with a few users more than 20% of load is achieved.

CAPACITY OF MIMO SYSTEMS IN 3G MICRO- AND PICOCELLS BASED ON DIRECTIONAL CHANNEL MODEL SIMULATIONS

[1,2]Pedro Vieira, [2]António Rodrigues

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal; [2]Instituto das Telecomunicações (IT) / Instituto Superior Técnico

Publicado em: *Proceedings of Progress in Electromagnetics Research Symposium 2003, Honolulu, USA, Outubro de 2003, pp.171.*

The capacity increase available from deploying multiple antennas at both the MS and the BS, has generated considerable interest in recent years. The capacity variations on the multiple-input/multiple-output (MIMO) radio channel will be simulated using the COST 259 Directional Channel Model as a tool to predict the radio environment. This will be done for two different 3GPP scenarios, exploiting the micro- and picocell case.

COST 259 DCM was implemented in MATLAB, for the two cell types (microcell and picocell). The model was developed using a modular structure, based on a certain number of properties implemented in the following order: cluster generation, cluster time and angular dispersion calculations, path-loss calculation using cell type dependent path-loss models, large-scale and small-scale fading implementation and finally the multi-path components (MPCs) definition (delay, angle, power amplitude and phase). This allows the user to obtain the directional channel impulse response (DCIR).

The 3GPP recommendations in were followed and were implemented two environments, micro- and picocell.

The MIMO capacity dependence on the SNR when the water filling power allocation scheme is used was also tested. Two antenna setups, a 4x4 and a 2x4 were compared.

Some conclusions can be drawn: the capacity increases with SNR and with the channel decorrelation. As the channel decorrelation increases, the 4x4 antenna configuration takes full advantage of its additional sub-channel compared with the 2x4, i.e., in the picocell scenario the capacity increase with SNR is larger than in the microcell scenario.

In this paper a stochastic MIMO radio channel model has been introduced using the multi-environment COST 259 directional channel model. The advantage of the proposed model is that it relies on a well structured and measurement tuned channel model, which reflects and predicts in a realistic way the main propagation behavior for different scenarios. As such, it can be used for link-level simulation studies.

CAPACITY OF MIMO SYSTEMS BASED IN 3G MICRO- AND PICOCELLS

[1,2]Pedro Vieira, [2]António Rodrigues

[1]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal; [2] Instituto das Telecomunicações (IT) / Instituto Superior Técnico

Publicado em:_*Proceedings of 6th International Symposium of Wireless Personal Multimedia Communications 2003, Yokosuka, Japão, Outubro de 2003, V2 pp 430-434.*

Capacity of MIMO (multiple-input/multiple-output) systems based on COST 259 channel model simulations are presented in this paper, for two different radio environments, micro- and picocell. Two different power allocation strategies are considered, “water filling” and uniform with different antenna topologies, 2x4, 3x4 and 4x4.

It is shown that MIMO usage is an efficient technique mainly in the picocell scenario, achieving capacities of 17 bit/s/Hz for 50% outage levels. In this case a 4x4 antenna configuration was used implementing water-filling at a SNR of 20 dB.

Considering MIMO application to UMTS system, half of the wavelength spacing between elements maximizes capacity considering SNR and MS size limitations. The number of antenna elements at the MS will depend on the mobile equipment characteristics.

MOVING TARGET DETECTION AND TRAJECTORY ESTIMATION USING A SINGLE SAR SENSOR"

[1]Dias and [1, 2]P. Marques

[1] Instituto Instituto Superior Técnico, Lisboa, Portugal;
[2]Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores., ISEL, Lisboa, Portugal;

Publicado em: *IEEE Transactions on Aerospace and Electronic Systems, vol. 39, no. 2, pp. 604-624, 2003*

The paper presents a novel methodology for determining the velocity and location of multiple moving targets using a single stripmap synthetic aperture radar (SAR) sensor. The so-called azimuth position uncertainty problem is therefore solved. The method exploits the structure of the amplitude and phase modulations of the returned echo from a moving target in the Fourier domain. A crucial step in the whole processing scheme is a matched filtering, depending on the moving target parameters, that simultaneously accounts for range migration and compresses two-dimensional signatures into one-dimensional ones without loosing moving target information. A generalized likelihood ratio test approach is adopted to detect moving targets and derive their trajectory parameters. The effectiveness of the method is illustrated with synthetic and real data covering a wide range of targets velocities and signal to clutter ratios (SCRs). Even in the case of parallel to platform moving target motion, the most unfavorable scenario, the proposed method yields good results for, roughly, SCR> 10 dB.

WHAT CAN WE LEARN FROM A MEASUREMENT OF SIN(2 BETA + GAMMA)?

J. P. Silva[a], A. Soffer[b], L. Wolfenstein[c], F. Wu[c]

[a] Área Científica de Física, ISEL, Lisboa, Portugal;
[b] Stanford Linear Accelerator Centre, Stanford, CA, U. S. A.;
[c] Departament of Phhysics, Carnegie Melllon University, Pittsburgh, PA, U. S. A.

Publicado em: *Physical Review D, Vol. 67, 036004 (2003).*

The constraints on the value of the CKM phase gamma that may be achieved by prospective measurements of sin(2 beta) and sin(2 beta + gamma) are discussed. Significant constraints require quite small errors, and may depend on assumptions about strong phases. The measurement of sin(2 beta + gamma) combined with other experiments could provide valuable limits on new physics in Bd-Bdbar mixing.

GENERAL DISCUSSION OF FUTURE ACTIVITIES

J. P. Silva

Área Científica de Física, ISEL, Lisboa, Portugal

Publicado em: *Livro Electrónico de Resumos do Workshop on the CKM Unitarity Triangle, Durham, U.K., Abril 2003.*

We summarize possible avenues for the future analysis of the constraints imposed by the CKM measurements on general classes of models of new physics. (Invited parallel session)

SUMMARY OF WORKING GROUP III

A. Buras[a], F. Parodi[b], J. P. Silva[c]

[a] Technical University Munich, Munich, Germany;

[b] Dipartimento di Física, Génova, Italia;
[c] Área Científica de Física, ISEL, Lisboa, Portugal

Publicado em: *Livro Electrónico de Resumos do Workshop on the CKM Unitarity Triangle, Durham, U.K., Abril 2003.*

We summarize the activities of working group III, which took place during the 2nd Workshop on the CKM Unitarity Triangle held in Durham in April 2003. (Invited final plenary session)

WEAK DECAYS, CP VIOLATION AND CKM: THEORETICAL STATUS

J. P. Silva
Área Científica de Física, ISEL, Lisboa, Portugal

Publicado em: *Livro Electrónico de Resumos do 19th International Workshop on Weak Interactions and Neutrinos, Lake Geneva, WI, U.S.A., Outubro 2003.*

We summarize the current status of the fields of Weak decays, CP violation and CKM. (Invited review plenary session)

FORCES BETWEEN ELONGATED PARTICLES IN A NEMATC COLLOID

D. Andrienko[a], M. Tasinkevych[b], P. Patricio[b, c], M. P. Allen[d], and M. M. Telo da Gama[b]
[a] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
[b] Centro de Física Teóretica e Computacional, Universidade de Lisboa, Avenida Professor Gama Pinto 2, P-1649-003 Lisboa Codex, Portugal
[c] Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro 1, P-1949-014 Lisboa, Portugal
[d] Center for Scientific Computing, University of Warwick, Coventry, United Kingdom

Publicado em: *Physical Review E, Vol. 68, 051702 (2003).*

Using molecular dynamics simulations we study the interactions between elongated colloidal particles (length to breath ratio>>1) in a nematic host.

The simulation results are compared to the results of a Landau–de Gennes elastic free energy. We find that depletion forces dominate for the sizes of the colloidal particles studied. The tangential component of the force, however, allows us to resolve the elastic contribution to the total interaction. We find that this contribution differs from the quadrupolar interaction predicted at large separations. The difference is due to the presence of nonlinear effects, namely, the change in the positions and structure of the defects and their annihilation at small separations.

Rheological properties of lyotropic solutions of acetoxypropylcellulose in dimethylacetamide. A comparision with the thermotropic case

M. T. Cidade[a] and C. R. Leal[b]

[a] Departamento de Ciência dos Materiais and CENIMAT, FCT/UNL, Caparica, Portugal;

[b] Área Científica de Física, ISEL, Lisboa, Portugal.

Publicado em: *Molecular Crystal and Liquid Crystals, 404, 95 (2003).*

The rheological properties of a thermotropic acetoxypropylcellulose (APC), were already described in previous works. In this work we present the rheological properties, viscosity, h, and first normal stress diference, N_1, of lyotropic solutions of APC in dimethylacetamide (DMAc).

The flow curve of the lyotropic solution presents the typical behaviour for this type of systems (Onogi and Asada Curve), however, contrary to what happens with other lyotropic systems, the APC/DMAc system presents a continuous increase of N_1 in function of the shear rate, which we attribute to the fact that APC has higher flexibility than the other liquid crystalline polymers studied so far, namely hydroxypropylcellulose and poly-benzyl-L-glutamate, that present a negative N_1 region, as well as to it's low molecular weight.

We will also present some remarks concerning rheo-optical studies preformed with APC/DMAc, by comparison with previous studies on thermotropic APC.

Rheological, morphological and mechanical properties of in situ compatibilized PP/Rodrun LC3000 blends

S. Filipe[a], J. M. Maia[a], C. R. Leal[c], A. Duarte[d] and M. T. Cidade[b]

[a] University of Minho, Polymer Engineering Department, Guimarães, Portugal;
[b] Materials Science Department and CENIMAT, FCT/UNL, Caparica, Portugal;
[c] Scientific Area of Physics, ISEL, Lisboa, Portugal and C.F.M.C.- Lisbon University, Portugal;
[d] ICTPOL, IST – Chemical Department, Lisboa, Portugal

Publicado em: *Livro de resumos da "AERC2003", 1st Anual European Rheology Conference, Universidade do Minho, Campus de Azurém, Guimarães, Setembro de 2003.*

The formation of reinforced thermoplastics can be easily obtained by the addition of liquid crystalline polymers. During extrusion, these materials are subjected to extensional forces, giving rise to the formation of oriented structures, which are retained after processing, thus leading to the formation of reinforced *in situ* composites. The mechanical properties of these blends are greatly enhanced, especially in the flow direction. The lack of adhesion between the thermoplastic and the liquid crystalline polymer is disadvantageous, but can be overcome by the addition of compatibilizers.

The effect of the addition of four different compatibilizers on the morphological and mechanical properties of liquid crystalline polymer and thermoplastic blends was studied. Three different compatibilizers were synthesized. These compatibilizers are mostly linear structures, part of the backbone being compatible with the polyolefin (matrix) and the other part with a liquid crystal compatible polyester structure. Varying the size and composition of these two segments, it was possible to vary the compatibility with each one of the components of the blend. The fourth compatibilizer is a commercial maleic anhydride-grafted polypropylene. The main objective of this work is to look for the best compatibilizer, *i.e.*, the one that leads to better mechanical properties of the compatibilized blend. The tensile properties of these blends were improved by the addition of compatibilizers, whereas the impact strength was not.

Rheology of latex / lyotropic liquid crystal suspensions

C. R. Leal[a] and M. T. Cidade[b]
[a] Área Científica de Física, ISEL, Lisboa, Portugal and C.F.M.C.- Univ. Lisboa, Lisboa, Portugal;
[b] Departamento de Ciência dos Materiais and CENIMAT, FCT/UNL, Caparica, Portugal

Publicado em: *Livro de resumos da 6th Ibero-American Workshop on Complex Fluids and their Applications, Lisboa, Portugal, Setembro de 2003.*

The lyotropic liquid crystal, potassium laurate, decylammonium chloride and water, is known to present two uniaxial phases (nematic and discotic) and a biaxial nematic phase.

Colloidal suspensions of latex particles (90 nm diameter) in this lyotropic liquid crystal have been systematically studied by A. Alves and E.A. Oliveira who established its phase diagram by means of polarised optical microscopy and birefringence measurements.

Based on this phase diagram, the rheological characterization of this system has been performed and the results are the aim of this presentation.

The viscosity vs shear rate curves will be presented for 0, 0.25, 0.5 and 1 wt % of latex particles (Rhodopás SA 128 is used, which is an anionic aqueous dispersion of carboxilated acrylic-styrene copolymer) and for temperatures that goes from 20 ºC (nematic calamitic phase) over 50 ºC (isotropic phase).

The influence of the latex particles content, in each phase, and the possibility of the establishment of the phase diagram by rheological means will be discussed.

KrF LASER CVD OF CHROMIUM OXIDE BY PHOTODEPOSITION OF $Cr(CO)_6$

P. M. Sousa[a], A. J. Silvestre[b], N. Popovici[a], M. L. Paramês[a], O. Conde[a]

[a] Departamento de Física, Faculdade de Ciências da Universidade de Lisboa;

[b] Instituto Superior de Engenharia de Lisboa

Publicado em: *Livro de resumos da conferência "Materiais 2003", 2nd International Materials Symposium, Costa da Caparica, Portugal, 2003 (comunicação oral).*

The prospect of building spintronic devices, in which electron spins are used to store and transport information, has attracted considerable attention in recent years. Many of these proposed devices demand carefully-controlled growth of ferromagnetic/insulator or ferromagnetic/semiconductor interfaces, the development of these interfaces being one of the main technological challenges to be overcome before realistic devices can be fabricated. Chromium dioxide (CrO_2) is an attractive compound to use in these heterostructures since it is strongly ferromagnetic at room temperature and has a half-metallic band structure fully spin-polarised at the Fermi level. Therefore, much effort has gone into developing efficient and controlled methods for preparing CrO_2 films at sufficiently low temperatures, which are of crucial importance to ensure interface quality and the ability to coat thermal-sensitive substrates such as those envisaged for building spintronic devices. Nevertheless, the synthesis of CrO_2 films at low temperatures has been a difficult task due to the metastable nature of this oxide. Laser-assisted CVD is a selective area deposition technique which has the potential to meet the requirements stated above.

This work reports on the synthesis of chromium oxide thin films prepared by photodissociation of $Cr(CO)_6$ in an oxidizing atmosphere, using a pulsed UV laser (KrF, $\lambda = 248$ nm). The experimental conditions which should enable the synthesis of CrO_2 are discussed and preliminary results on the synthesis of Cr_xO_y films on Si (100) and Al_2O_3 (0001) substrates are presented.

KrF PULSED LASER DEPOSITION OF CHROMIUM OXIDE THIN FILMS FROM Cr_8O_{21} TARGETS

N. Popovici[a], M. L. Paramês[a], P.M. Sousa[a], A. J. Silvestre[b], O. Conde[a]

[a] Departamento de Física, Faculdade de Ciências da Universidade de Lisboa;

[b] Instituto Superior de Engenharia de Lisboa

Publicado em: *Livro de resumos da conferência "COLA'03", 7th International Conference on Laser Ablation, Hernissos, Crete, Greece, 2003 (comunicação oral).*

Chromium dioxide (CrO_2) is an attractive compound to be used in spintronic heterostructures since it is strongly ferromagnetic at room temperature ($T_c = 393$ K) and has a half-metallic band structure fully spin-polarised at the Fermi level. However, and despite the efforts that have been put into developing efficient and controlled methods for preparing CrO_2 films, their synthesis at low temperatures has been a difficult task due to the metastable nature of this oxide. This is indeed essential to ensure interface quality and the ability to coat thermal-sensitive materials such as those envisaged in spintronic devices. Pulsed Laser Deposition (PLD) is a technique that has the potential to meet the requirements stated above.

In this work, we describe our efforts to grow chromium oxide thin films by PLD from Cr_2O_3 and Cr_8O_{21} targets, and using a KrF excimer laser. The chemical composition of the samples was evaluated by Rutherford backscattering (RBS) measurements, and their surface topography was studied by atomic force microscopy (AFM). X-ray diffraction performed at glancing incidence angle (GIXRD) was used for phase analysis showing that chromium oxides exhibiting different stoichiometries may be formed depending on processing parameters - oxygen background pressure and laser fluence. Microstructural characterisation was complemented by using micro-Raman spectroscopy, which showed evidence of co-deposition of CrO_2 and Cr_2O_3 in a number of the deposited thin films.

Fe_3O_4 THIN FILMS DEPOSITED ON Si SUBSTRATES BY PLD

N. Popovici[a], M. L. Paramês[a], P. M. Sousa[a], A. J. Silvestre[b], O. Conde[a]

[a] Departamento de Física, Faculdade de Ciências da Universidade de Lisboa;

[b] Instituto Superior de Engenharia de Lisboa

Publicado em: *Livro de resumos da conferência "Materiais 2003", 2nd International Materials Symposium, Costa da Caparica, Portugal, 2003 (comunicação oral).*

Magnetite (Fe_3O_4) is one of the most studied ferrimagnetic materials due to its unique electrical and magnetic properties. Thin films of magnetite can advantageously replace bulk material in its current applications and also give the possibility of controlling transport and magnetic properties depending on the colleting material, thickness, morphology and microstructure. Current applications include recording-head, magnetoptical and magnetoresistance applications.

Different techniques have been used to growth high quality Fe_3O_4 thin films, on a variety of substrates, in particular Pulsed Laser Deposition (PLD). However, it is still difficult to grow iron oxide thin filmshaving well defined surface composition and microstructure. Especially, thin films grown at high temperature generally consist of multi-phase domains. Precise control of the deposition variables is critical to grow well defined iron oxide films. In this work ablation of Fe_3O_4 targets (contaminated with Fe_2O_3) was performed using a pulsed UV laser (KrF, 248 nm). The ablated material was deposited onto Si (100) substrates, at room temperature. Different experimental conditions were essayed in order to optimize the parameters for the control of the properties of the deposited films. Preliminary results of pulsed laser deposited Fe_3O_4 thin films formed in UHV and O_2 reactive atmosphere, for different laser fluences, will presented regarding their structural, chemical and microstructural properties.

IRON OXIDE THIN FILMS GROWN BY PULSED LASER DEPOSITION

M. L. Paramês[a], N. Popovici[a], P. M. Sousa[a], A. J. Silvestre[b], O. Conde[a]

[a] Departamento de Física, Faculdade de Ciências da Universidade de Lisboa;

[b] Instituto Superior de Engenharia de Lisboa

Publicado em: *Livro de resumos da conferência “APHYS 2003”, 1st International Meeting on Applied Physics, Badajoz, Spain, 2003 (Poster).*

Magnetite (Fe_3O_4) is an attractive compound to be used in magnetotransport applications since it has a predicted half-metallic band structure fully spin-polarised at the Fermi level and it has a very high Curie temperature (~860 K). Different techniques have been used to grow Fe_3O_4 thin films on a variety of substrates, in particular pulsed laser deposition (PLD). However, and despite the efforts that have been put into developing efficient and controlled methods for preparing Fe_3O_4

films, it is still difficult to grow them with a controlled and well defined composition and microstructure.

In this work, ablation of Fe_3O_4 targets (contaminated with α-Fe_2O_3) was performed using a pulsed UV laser (KrF, $\lambda = 248$ nm). The ablated material was deposited onto Si (100) substrates and different experimental conditions were tested in order to optimise the parameters that allow for control of the properties of the deposited iron oxide. Results of films grown in high vacuum ($1\text{–}3\times10^{-5}$ mbar), inert (Ar) and O_2 reactive atmospheres, for different laser fluences, will be presented regarding their structural, chemical and microstructural properties.

ANISOTROPIC TOMOGRAPHY OF THE ATLANTIC OCEAN

G. Silveira[a,b], E. Stutzmann[c]

[a] Centro de Geofísica da Universidade de Lisboa, Lisboa, Portugal;
[b] Área Científica de Física, ISEL, Lisboa, Portugal E-mail: gsilveira@dem.isel.ipl.pt;
[c] Institut de Physique du Globe de Paris, Paris, França

Publicado em: *Geophysical Research Abstracts, Vol. 5, 03859 (2003)*
European Geophysical Society

We present a regional tri-dimensional model of the Atlantic Ocean with anisotropy. The model, derived from Rayleigh and Love phase velocity measurements, is defined from the Moho down to 300 km depth with a lateral resolution of about 500 km and is presented in terms of average isotropic S-wave velocity, azimuthal anisotropy and transverse isotropy. The cratons beneath North America, Brazil and Africa are clearly associated with fast S-wave velocity anomalies. The Mid Atlantic Ridge is a shallow structure in the North Atlantic corresponding to a negative velocity anomaly down to about 150 km depth. In contrast, the ridge negative signature is visible in the South Atlantic down to the deepest depth inverted, that is 300 km depth. This difference is probably related to the presence of hot-spots along or close to the ridge axis in the South Atlantic and may indicate a different mechanism for the ridge between the North and South Atlantic. Negative velocity anomalies are clearly associated with hotspots from the surface down to at least 300 km depth, they are much broader that the supposed size of the hot-spots and seem to be connected along a North-South direction. Down to 100 km depth, a

fast S-wave velocity anomaly is extenting from Africa into the Atlantic Ocean within the zone defined as the Africa superswell area. This result indicates that the hot material rising from below does not reach the surface in this area but may be pushing the lithosphere upward. In most parts of the Atlantic, the azimuthal anisotropy directions remain stable with increasing depth. Close to the ridge, the fast S-wave velocity direction is roughly parallel to the sea floor spreading direction. The hot-spot anisotropy signature is striking beneath Bermuda, Cape Verde and Fernando Noronha islands where the fast S-wave velocity direction seems to diverge radially from the hot-spots. The Atlantic average radial anisotropy is similar to that of the PREM model, that is positive down to about 220 km, but with slightly smaller amplitude and null deeper. Cratons have a lower than average radial anisotropy. As for the velocities, there is a difference between North and South Atlantic. Most hot-spots and the South Atlantic ridge are associated with positive radial anisotropy perturbation whereas the North Atlantic ridge corresponds to negative radial anisotropy perturbation.

PLUME RIDGE LITHSPHERIC INTERACTIONS: CASES OF AFAR (AFRICA), AZORES (ATLANTIC), AND PACIFIC

J. P. Montagner[a], E. Stutzmann[a], D. Sicilia[a], A. Sebai[a], E. Beucler[a], G. Silveira[b,c], M. Cara[d], E. Debayle[d], J. J. Lévêque[d]

[a] Institut de Physique du Globe de Paris, Paris, França;
[b] Centro de Geofísica da Universidade de Lisboa, Lisboa, Portugal;
[c] Área Científica de Física, ISEL, Lisboa, Portugal E-mail: gsilveira@dem.isel.ipl.pt;
[d] EOST, Université Louis Pasteur, Strasbourg, France.

Publicado em: *Geophysical Research Abstracts, Vol. 5, 08080 (2003)*
European Geophysical Society

Detection of mantle plumes in geophysical and geochemical data is controversial and trigger vigorous debates. It remains unclear how plumes are formed, their origin at depth, and whether they act independently from plate tectonics. We may learn about the role of plumes in mantle dynamics by studying their interactions with lithosphere and crust below ridges and the way in which they perturb the flow pattern in the uppermost mantle. Regional tomographic studies of

seismic velocity and anisotropy around several hotspots were obtained during the last 2 years. Their lateral resolution is smaller than 1000 km and they enable to make qualitative intercomparison between Afar (Horn of Africa Program), Azores (COSEA project) in the Atlantic, La Reunion in the Indian Ocean and Pacific provinces hotspots. These models demonstrate that there is not only one family of plumes but several ones. Some plumes are confined in the uppermost 200 km but a few can originate in the transition zone and even at the Core-mantle Boundary for superplumes. Seismic anisotropy which is a good marker of deformation processes and mantle flow pattern shows that the interaction between a plume and a ridge below the lithosphere can occur over distances larger than 1000 km, via sublithospheric channels. The existence of LACs (Low Anisotropy Channels) below the Pacific plate seems to be intimately related to the active hotspots in Central Pacific and indicate a future reorganization of plate boundaries

AZORES HOTSPOT DEEP SIGNATURE

G. Silveira[a,b], E. Stutzmann[c], A. Davaille[c], J. Montagner[c], L. M. Victor[d]

[a] Centro de Geofísica da Universidade de Lisboa, Lisboa, Portugal;
[b] Área Científica de Física, ISEL, Lisboa, Portugal E-mail: gsilveira@dem.isel.ipl.pt;
[c] Institut de Physique du Globe de Paris, Paris, França;
[d] Instituto Geofísico do Infante D. Luís, Lisboa, Portugal

Publicado em: *Livro de Resumos do 2003 AGU FALL MEETING, San Francisco, USA, 8-12 Dezembro de 2003.*

The Azores archipelago occupies a lateral branch of the Mid-Atlantic ridge near the triple junction of 3 large tectonic plates. The tectonic setting is even more complex due to the existence of the Azores hotspot and to the hotspot-ridge interaction. But the hotspot origin at depth as a plume and its lateral extent are controversial subjects. High-resolution tomographic models can provide an important hint to evaluate the depth and lateral extent of mantle plumes. We investigate the Azores deep seismic structure as seen on recent global and regional studies. The mapping of S-wave negative velocity anomalies in the different models reveals that the anomaly right beneath the Azores seems to be confined in the upper 200 km. Considering the time evolution of a plume, this low velocity anomaly might be the signature of a present-day dying plume, that created the Azores plateau 20 Ma ago. In Silveira and Stutzmann (2002), the negative velocity anomaly beneath the Azores archipelago seems to be connected to a deep anomaly further at the South. This deep anomaly (28ºN/26ºW, 200-400 km) is in the middle of the bunch of Azores, Great Meteor, Madeira and Canary hotspots, and might be related to a plume originating either in the transition zone or in the lower mantle. This single deep plume is located too far from the Azores archipelago for being responsible of the Azores plateau formation. But, due to the lithosphere geometry, this single plume might feed at present day Azores, Great Meteor, Madeira, Canaries and Cape Verde hotspots and therefore be at the origin of the present day volcanism. The diverging azimuthal anisotropy around this point below lithosphere is confirming a unique origin of these hotspots.

AZORES CRUSTAL STRUCTURE DERIVED FROM RECEIVER FUNCTIONS

P. Silva[a], G. Silveira[a,b], N. Lourenço[a], E. Stutzmann[c], M. Miranda[a]

[a] Centro de Geofísica da Universidade de Lisboa, Lisboa, Portugal;
[b] Área Científica de Física, ISEL, Lisboa, Portugal E-mail: gsilveira@dem.isel.ipl.pt;
[c] Institut de Physique du Globe de Paris, Paris, França

Publicado em: *Livro de Resumos do 2003 AGU FALL MEETING, San Francisco, USA, 8-12 Dezembro de 2003.*

During the last two decades efforts have been put together to understand the processes responsible for the Azores plateau formation. The geodynamics of this plateau, located at the triple junction between America, Africa and European plates, is dominated by the tectonics of the triple junction and by hotspot activity. But, the relationship between islands volcanism and a possible plume beneath the Azores is still not well understood and the triple junction exact location is also under debate.

From October 2000 to September 2002, temporary broadband seismic stations have been deployed in the Azores archipelago in the framework of the COSEA Memoradum of Understanding. These broadband data have been used to compute receiver functions and estimate the crustal structure beneath the islands.

Radial receiver functions where analysed by both inverse and forward modelling in order to obtain 1-D S-wave profile. Crustal receiver functions exhibit local effects and the stations can be separated into 2 groups. Flores and Corvo islands, that are located at the west of the ridge axis and central islands (Faial and Pico) display slow crustal S-wave velocity whereas the eastern island of Santa Maria is associated with fast crustal S-wave velocity. These results will be discussed in the Azores geodynamic context.

FABRICS MAGNÉTICOS E MAGMÁTICOS EM DIQUES: CONCORDÂNCIAS E DISCREPÂNCIAS.

M. Moreira[a,b], C. R. Nogueira[c], P. Terrinha[c,d]

[a] Instituto Superior de Engenharia de Lisboa, R. Cons. Emídio Navarro, 1, 1949-014 Lisboa, Portugal;
[b] Centro de Geofísica da Universidade de Lisboa, Ed. C8, 1749-016 Lisboa, Portugal;
[c] LATTEX, Faculdade de Ciências, Universidade de Lisboa, Ed. C2, 5º Piso, 1749-016 Lisboa, Portugal;
[d] Departamento de Geologia, Faculdade de Ciências, Universidade de Lisboa, Ed. C2, 5º Piso, 1749-016 Lisboa, Portugal

Publicado em: *Ciências da Terra – Número Especial V, p53, VI Congresso Nacional de Geologia, Departamento de Ciências da Terra, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Junho 2003.*

Em diques basálticos a lineação magnética, eixo k1 do elipsóide de anisotropia da susceptibilidade magnética, é usualmente associado à direcção do escoamento magmático, contemporâneo com os estados finais de arrefecimento do magma. Esta hipótese foi testada em diques do Cortejo Radial de Diques de Mafra através de comparações entre os fabrics magnético e magmático. Através da análise de imagem sobre lâminas delgadas cortadas segundo os planos k1-k2 e k1-k3 foram obtidas as orientações preferenciais dos minerais opacos (óxidos de Fe, Ti) e plagioclases, estas últimas assumidas como indicadoras da direcção média do escoamento magmático. A análise dos resultados mostrou que em 53% dos casos o afastamento angular das plagioclases relativamente à direcção de k1 é inferior a 15° e em 40 % dos casos o afastamento é superior a 60°.

Este comportamento bimodal sugere que a associação directa do eixo k1 ao escoamento magmático poderá, em numerosos casos, ser incorrecta. Assim, propõe-se um método essencialmente geométrico que permite a determinação completa de um vector de escoamento magmático (direcção e sentido) que não se baseia na utilização única da lineação magnética como indicador de escoamento, mas sim na utilização do plano de foliação magnética, plano k1-k2, e do ângulo de imbricação, relativamente a cada margem.

FLUXO MAGMÁTICO EM DIQUES DO CORTEJO RADIAL DE DIQUES DE MAFRA.

C. R. Nogueira[c], M. Moreira[a,b], P. Terrinha [c,d]

[a] Instituto Superior de Engenharia de Lisboa, R. Cons. Emídio Navarro, 1, 1949-014 Lisboa, Portugal;
[b] Centro de Geofísica da Universidade de Lisboa, Ed. C8, 1749-016 Lisboa, Portugal;
[c] LATTEX, Faculdade de Ciências, Universidade de Lisboa, Ed. C2, 5º Piso, 1749-016 Lisboa, Portugal;
[d] Departamento de Geologia, Faculdade de Ciências, Universidade de Lisboa, Ed. C2, 5º Piso, 1749-016 Lisboa, Portugal.

Publicado em: *Ciências da Terra – Número Especial V, p53, VI Congresso Nacional de Geologia, Departamento de Ciências da Terra, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Junho 2003.*

Apresenta-se um estudo comparativo de resultados obtidos de anisotropia de susceptibilidade magnética ASM, da orientação de vesículas gasosas e da orientação preferencial de formas em cerca de 200 amostras de 7 diques basálticos do cortejo radial de Mafra.

Conclui-se que existe concordância entre a orientação da ASM e das vesículas gasosas, controlada pela orientação do fluxo magmático. Os dados experimentais mostram que: (1) convergência dos eixos k3 da ASM nos pólos do dique; (2) fabric magnético essencialmente triaxial, definindo planos de foliação magnética, quase-paralelos ao plano do dique; (3) coerência nos ângulos de imbricação dos planos de foliação

magnética, nos vário diques, possibilitando a determinação de um sentido de fluxo magmático.

A assimetria sistemática dos ângulos de imbricação entre as margens Norte e Sul, sugerem um campo de tensões triaxial, contemporâneo com a instalação dos diques.

POLARIZAÇÃO DE ONDAS S DA SEQUÊNCIA SÍSMICA DO FAIAL DE 1998-7-9

Nuno A. Dias[a,b], Luis Matias[a,c], Julia Téllez[d], L. Senos[e], J. L. Gaspar[f], D. Vales[e]

[a] Centro de Geofísica da Universidade de Lisboa;

[b] Instituto Superior de Engenharia de Lisboa;

[c] Faculdade de Ciências da Universidade de Lisboa;

[d] Universidad Complutense de Madrid;

[e] Instituto de Meteorologia;

[f] Centro de Vulcanologia da Universidade dos Açores.

Publicado em: *Livro de Resumos do 3º Simpósio de Meteorologia e Geofísica da APMG, Aveiro, Portugal, Fevereiro de 2003*

Efectuou-se uma re-análise do conjunto de 112 eventos analisados no trabalho de Dias et al. (2002), recorrendo a polarigramas e ao método da matriz da covariância. O método da matriz da covariância, sendo mais robusto e quantificando melhor a distribuição de energia no sinal, revelou uma polarização geralmente pouco estável, possivelmente indiciando uma anisotropia mais complexa que a proposta pelo modelo *EDA* de Crampin. O conjunto de dados revelou alguns problemas: baixa cobertura azimutal para o conjunto das estações, desconhecimento do mecanismo focal de alguns dos eventos (não permitindo destrinçar os efeitos associados à fonte dos devidos à estrutura sob a estação) e marcações incorrectas de fases, devido à presença de conversões. Esta última afectou principalmente a marcação das fases S, objecto do estudo, ocorrendo com frequência a presença de uma fase percursora da S. O recurso aos polarigramas, mostrou que esta fase se trataria de uma onda convertida devido à presença de energia na componente vertical, por vezes mais forte que na componente horizontal.

SHEAR-WAVE POLARIZATION ANALYSIS OF THE SEISMIC SWARM FOLLOWING THE JULY 9th 1998 FAIAL (AZORES) EARTHQUAKE

Nuno A. Dias[a,b], Luis Matias[a,c], Julia Téllez[d], L. Senos[e], J. L. Gaspar[f]

[a] Centro de Geofísica da Universidade de Lisboa;

[b] Instituto Superior de Engenharia de Lisboa;

[c] Faculdade de Ciências da Universidade de Lisboa;

[d] Universidad Complutense de Madrid;

[e] Instituto de Meteorologia;

[f] Centro de Vulcanologia da Universidade dos Açores.

Publicado em: *Geophysical Research Abstracts, Vol. 5, 07002, EGS-AGU-EUG Joint Assembly, Nice, Abril de 2003*

On July 9th 1998 an Mw = 6.2 earthquake stroked the island of Faial, in the central group of the Azores archipelago, followed by a seismic. The preliminary results of the shear-wave polarization analysis of a selected dataset of events of this swarm (112 best-constrained events), recorded in the first 2 weeks on the 3 islands surrounding the area of the main shock. The aim was to analyse the behaviour of the S wave polarization and the relationship with seismic anisotropy under the seismic stations, and its correlation with the regional structure. The polarization direction observed in the majority of the seismic stations is not stable, varying from SE-NW to WSW-ENE, and showing also the presence in same cases of shear-wave splitting, indicating the presence of anisotropy. Part of the polarization seems to be coherent with the direction of the local tectonic features, but its instability suggest a more complex seismic anisotropy than that proposed by the model EDA of Crampin.

Título. Multi-Objective Topology Optimization Of Structures

Autores. J. F. Aguilar Madeira[1,2]

Filiações: [1]Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: Jaguilar@isel.pt; [2]Departamento de Engenharia Mecânica, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, Portugal.

Publicado em: The Sixth International Conference on Computational Structures Technology– *Prague- Czech Republic.*

The topology optimization problem of structures can be viewed as the process of identifying solid or void regions within an allowed domain, in order to obtain the optimal structure topology for given criterion and a given amount of material.

This problem, as stated above, is an integer programming problem (material/no-material) difficult to solve by classical programming methods. To overcome this difficulty a relaxation of the problem is possible, by introducing a material volume fraction parameter that has a continuous variation from zero to one.

Alternatively, the binary chromosome design storage and global search capabilities of the Genetic Algorithm (GA) make it a powerful tool for solving topology design problem. Due to the equality constraint on volume, here considered, all the chromosomes used in the GA lead to the same volume value, hence all of them have the same number of ones (implicitly, the same number of zeros) along the evolutionary process.

For a typical chromosome defined by L genes, we have a total of 2^L possible solution, in the representation scheme. Considering the volume equality constraint, a significant reduction in this number can be achieved. If a L genes chromosome is consider, with K genes being one (1<K<L), we will only have $C_K^L = \frac{L!}{K!(L-K)!}$ possible variations. The present analysis explores this fact leading to a reduction in computational effort. To proceed in this way, it is necessary to define these chromosomes and to create new operators of crossover and mutation, that preserve volume.

In contrast to single-objective optimization, where objective and fitness functions are often identical, both fitness assignment and selection must allow for several objectives when multi-objective optimization problems are considered.

Hence, instead of a single optima, multi-objective optimization problems solution is often a family of points, known as Pareto optimal set, where each objective component of any point along the Pareto-front can only be improved by degrading at least one of its other objective components. In the total absence of information regarding the preferences of objectives, a ranking scheme based upon the Pareto optimality is regarded as an appropriate approach to represent the strength of each individual in an evolutionary algorithm for multi-objective optimization (Fonseca and Fleming, Srinivas and Deb).

Since a great diversity of solutions exists, additional information is introduced in the algorithm. This action leads to a reduction in the computational effort needed. The information supplied to the algorithm is obtained a priori from classical methods, regarding single-objective optimization, and the initial population individuals are derived from this information.

A very powerful tool the resolution of multi-objective problems is developed by considering the present alliance between genetic and classical methods. The computation model is tested in numerical applications.

Título. Multi-Objective Optimization Of Structures Topology by Genetic Algorithms

Autores. J. F. Aguilar Madeira[1,2], H. Rodrigues[2] e Heitor Pina[2]

Filiações: [1]Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: Jaguilar@isel.pt; [2]Departamento de Engenharia Mecânica, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, Portugal.

Publicado em: Evolutionary Multi-Criterion Optimization, Second International Conference, EMO 2003, Faro, Portugal, April 2003, Proceedings. Lecture Notes in Computer Science 2632 Springer 2003, ISBN 3-540-01869-7

This work develops a computational model for topology optimization of linear elastic structures for situations where more than one objective function is required, each one of them with a different optimal solution.

The method is thus developed for multi-objective optimization problems and is based on Genetic Algorithms. Its purpose is to evolve an evenly distributed group of solutions (population) to obtain the optimum Pareto set for the given problem.

To reduce computational effort, optimal solutions of each of the single-objective problems are introduced in the initial population.

Two numerical examples are presented and discussed to assess the method.

Título. Optimização Topológica Multi-objectivo de estruturas via algoritmos genéticos

Autores. J. F. Aguilar Madeira[1,2], H. Rodrigues[2] e Heitor Pina[2]

Filiações: [1]Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: Jaguilar@isel.pt; [2]Departamento de Engenharia Mecânica, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, Portugal.

Publicado em: VII Congresso Nacional de Mecânica Aplicada e Computacional, Universidade de Évora, Abril 2003

Neste trabalho é desenvolvido um modelo de optimização topológica multi-objectivo de estruturas lineares e elásticas através dos Algoritmos Genéticos (AG).

Quando se trabalha com problemas de optimização de topologia, é usual considerar um constrangimento sobre o volume disponível. Neste trabalho considerou-se um constrangimento de igualdade sobre o volume. Por causa deste constrangimento, todos os cromossomas utilizados no AG, população inicial e novos indivíduos determinados ao longo do processo evolutivo, têm o mesmo volume (número de "uns" e "zeros" é fixo). Para tal, cria-se uma população inicial de indivíduos com esta característica e para o processo evolutivo foram desenvolvidos novos operadores de cruzamento e mutação (que preservam o volume).

O método é desenvolvido para problemas de optimização multi-objectivo. Para os resolver utiliza-se um algoritmo que mantenha a diversidade da população na fronteira de Pareto e guie a busca na direcção do conjunto óptimo de Pareto.

Com o intuito de reduzir o esforço computacional, são introduzidas na população inicial as soluções óptimas de cada um dos objectivos considerados, tais soluções são determinadas pelos métodos clássicos.

Alguns dos resultados obtidos são comparados com os que se obtêm através dos métodos clássicos.

Título. Análise e Optimização de Apoios de Suspensão em Borracha

Autores. Ricardo Garcia Lage[1], Luís Oliveira Faria[1], Tomás Pedro Trigo[1] , J. F. Aguilar Madeira[1,2].

Filiações: [2]Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: Jaguilar@isel.pt; [1]Departamento de Engenharia Mecânica, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, Portugal.

Publicado em: VII Congresso Nacional de Mecânica Aplicada e Computacional, Universidade de Évora, Abril 2003

Os apoios de suspensão em borracha para automóveis têm a forma genérica de um cilindro de paredes espessas e são sujeitos a deformações de corte segundo o seu eixo. Variando esta forma, e procedendo à aplicação de uma pré-carga, tenta-se que estes componentes atinjam um comportamento mecânico especificado, em termos de rigidez axial e lateral, e de resistência a cargas máximas e de fadiga.

A análise do comportamento mecânico destes apoios é altamente não linear: grandes deformações, materiais elásticos não lineares, contacto entre corpos diferentes e entre partes do mesmo corpo. Para obter expressões analíticas que possibilitem uma análise preliminar é necessário simplificar o problema.

Em primeiro lugar consideramos que estes apoios têm a forma de um tubo cilíndrico longo de material elástico, incompressível e isotrópico, e que são sujeitos a uma (grande) deformação de corte axial. Existem soluções analíticas para este problema com vários tipos de leis constitutivas para borrachas (Ogden, 1973) e seleccionamos a mais simples com um material do tipo *neo-Hookean*.

No caso do tubo cilíndrico ser curto, a distribuição de tensões de corte varia ao longo do eixo e haverá tensões normais de flexão junto das superfícies livres. Neste caso não existe solução analítica não linear, e apresentamos expressões baseadas numa teoria linear de placas espessas. Verifica-se que a solução anterior é adequada, a não ser no caso de cilindros muito curtos.

Estas fórmulas permitem, com base num critério de vida à fadiga utilizado na indústria, estabelecer gráficos de utilização simples, adequados para o pré-dimensionamento de apoios.

Por último apresentamos um exemplo real de análise e optimização de um apoio de suspensão cuja simulação é complexa; nele se descreve a geometria detalhada da solução encontrada para o componente, evitando concentrações de tensão e instabilidades superficiais na borracha que reduzem a sua resistência e duração.

Título. Chromosome Repairing in Genetic Methods for Multi-Objective Topology Optimization Of Structures with an Equality Constraint on Volume

Autores. J. F. Aguilar Madeira[1,2], **H. Rodrigues[2] e Heitor Pina[2]**

Filiações: [1]Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: Jaguilar@isel.pt; [2]Departamento de Engenharia Mecânica, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, Portugal.

Publicado em: Fifth World Congress on Structural and Multidisciplinary Optimization, Lido di Jesolo- Venice, Maio de 2003.

As an equality constraint on volume as to be enforced, all chromosomes used in the genetic algorithm must generate individuals with the same volume value; in the coding adopted this means that they must preserve the same number of ones and, implicitly, the same number of zeros, along the evolutionary process. It is thus necessary to define these chromosomes, to create corresponding operators of crossover and mutation which preserve volume and to "repair" the chromosomes for admissible solutions.

The method is developed for multi-objective optimization problems. Its purpose is to evolve an evenly distributed group of solutions to determine the optimum Pareto set for a given problem. The algorithm determines a set of solutions (a population), this population being sorted by its domination properties and a filter is defined in order to retain the Pareto solutions.

To reduce computational effort, optimal solutions of each of the single-objective problems are introduced in the initial population.

Results obtained by the evolutionary and classical methods are compared.

Multi-Objective Optimization Of Structures Topology by Genetic Algorithms.

Autores. J. F. Aguilar Madeira[1,2], H. Rodrigues[2] e Heitor Pina[2]

Filiações: [1]Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: Jaguilar@isel.pt; [2]Departamento de Engenharia Mecânica, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, Portugal.

Publicado em: Aceite para publicação, Outubro de 2003, em "Advances in Engineering Software, Computer & Structures", Ref.:S2002/2002/000015.

This work develops a computational model for topology optimization of linear elastic structures for situations where more than one objective function is required, each one of them with a different optimal solution.

The method is thus developed for multi-objective optimization problems and is based on Genetic Algorithms. Its purpose is to evolve an evenly distributed group of solutions (population) to obtain the optimum Pareto set for the given problem.

To reduce computational effort, optimal solutions of each of the single-objective problems are introduced in the initial population.

Two numerical examples are presented and discussed to assess the method.

Título. Joint Regression Analysis and Connectdness Application to Grapewines.

Autores. João Tiago Mexia[1] , Iola Pinto[2]
Filiações:[1] Faculdade de Ciências e Tecnologia Departamento de Matemática Monte da Caparica, Portugal
[2]Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: iolapinto@sapo.pt

Publicado em:_Colloquium Biometryczne Tom 33, 2003 - Polónia

The use of Joint Regression Analysis technique, and L_2 environmental indexes allows the interpretation of experiments which were obtained independently, once satisfy the connectdness condition. It is shown how to deal with possible specific interactions. Application to two sets of experiments on closed related grapewines clones are given.

Título. Comparison of wheat cultivars in Portugal (1986-2000).

Autores. João Tiago Mexia[1] , Iola Pinto[2]
Filiações: [1] Faculdade de Ciências e Tecnologia Departamento de Matemática Monte da Caparica, Portugal
[2]Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: iolapinto@sapo.pt

Publicado em: Em apreciação para apresentação na Polónia e publicação na revista "Colloquium Biometryczne Tom 33, 2004"

Joint Regression Analysis is used to treat the results of wheat breeding in Portugal from 1986 to 2000.

Selected cultivars are found and the policy followed in the breeding program is discussed.

Título. CONNECTEDNESS AND L_2 ENVIRONMENTAL INDEXES APPLICATION TO GRAPEWINES.

Autores. João Tiago Mexia[1] , Iola Pinto[2]
Filiações: [1] Faculdade de Ciências e Tecnologia Departamento de Matemática Monte da Caparica, Portugal
[2] Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: iolapinto@sapo.pt

Publicado em:_Apresentado no Simpósio de Vitivinicultura de Julho de 2003. A publicar na revista "Acta Horticulturae da ISHS 2004"

Given a group of experiments designed separately it is shown how to check for connectedness and, if this condition holds, to use L_2 environmental indexes to carry out a Joint Regression Analysis. Two applications on experiments on grapewines of castes Aragonês and Arinto are carried out.

Título. WHEAT BREEDING PROGRESS IN PORTUGAL (1986-2000).

Autores. João Tiago Mexia[1] , Iola Pinto[2]
Filiações: [1] Faculdade de Ciências e Tecnologia Departamento de Matemática Monte da Caparica, Portugal
[2]Área Científica de Matemática, ISEL, Lisboa, Portugal E-mail: iolapinto@sapo.pt

Publicado em: Em apreciação para apresentação na Polónia e publicação na revista "Colloquium Biometryczne Tom 33, 2004"

The environmental index is a synthetic variable that measures the productivity per block in field experiments for cultivars comparison. Using the environmental indexes adjusted for the blocks in the Portuguese wheat breeding program (1986-2000), a linear model was adjusted. The explicative variables were: year, location and cultivars. Coefficients for cultivars corrected for the years and locations were obtained. The main result obtained was that the set of selected cultivars at the end of the program had significantly higher ($p < 0.1\%$) corrected coefficients.

Topological Entropy as a measure of Chaos in forced excitable systems

Jorge Duarte(a); J. Sousa Ramos(b)

(a) Área Científica de Matemática, Instituto Superior de Engenharia, R. Conselheiro Emídio Navarro 1, 1949-014 Lisboa, Portugal.

(b) Departamento de Matemática, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

Publicado em: *International Journal of Pure and Applied Mathematics, 4, 2 (2003) 165-181.*

Periodically-forced excitable systems arise in many biological and physiological applications. Chaotic dynamics of a forced piecewise-linear Fitzhugh-Nagumo-like system under large amplitude forcing was identified by Hans G. Othmer and Min Xie in their work (1999). In this paper we study the chaotic behavior of a special type of canonical return maps for a singular system, in some regions of parameter space. Using symbolic dynamics, in particular, some results concerning the Markov partitions associated to maps on the interval, we characterize the topological entropy of the singular system and we study the variation of this topological invariant with the parameters A, θ and T. This work is still another illustration of the role that the theory of dynamical systems can play in study of excitable systems.

TOPOLOGICAL INVARIANTs IN FORCED PIECEWISE-LINEAR FITZUGH-NAGUMO-LIKE SYSTEMS

Jorge Duarte[a]; J. Sousa Ramos[b]

[a]Área Científica de Matemática, Instituto Superior de Engenharia, R. Conselheiro Emídio Navarro 1, 1949-014 Lisboa, Portugal; [b]Departamento de Matemática, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

Palestra em: *Dynamical Systems Conference – Denton 2003, University of North Texas, USA, 25-29 Maio de 2003.*

Mathematical models for periodically-forced excitable systems arise in many biological and physiological contexts. Chaotic dynamics of a forced piecewise-linear Fitzhugh-Nagumo-like system under large-amplitude forcing was identified by Hans G. Othmer and Min Xie in their work. Using kneading theory we study the topological entropy of some chaotic return maps associated with a singular system. Finally we introduce a new topological invariant to distinguish isentropic dynamics.

DISCRETE DYNAMICS OF THE FITZHUGH-NAGUMO SYSTEMS

Jorge Duarte[a]; J. Sousa Ramos[b]

[a]Área Científica de Matemática, Instituto Superior de Engenharia, R. Conselheiro Emídio Navarro 1, 1949-014 Lisboa, Portugal; [b]Departamento de Matemática, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

Palestra em: *XIV International Congress on Mathematical Physics, Lisbon, July 28 – August 2, 2003.*

The Fitzhugh-Nagumo-like systems are well-know in physiology and they contributed enormously to the formation of a new field of applied mathematics, the study of excitable systems. We study the chaotic behavior of canonical return maps for a Fitzhugh-Nagumo system. Using bifurcation theory we characterize the dynamics, in particular some routes to chaos, in special regions of the parameter space.

CURRENT-PRESSURE-VOLTAGE CHARACTERISTICS IN A PLANAR MAGNETRON DISCHARGE

M. L. Escrivão[a]; P. J. S. Pereira[b]; M. H. Cabral[a] ; M. R. Teixeira[a] ; M. J. P. Maneira[a]

[a]CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Quinta da Torre, 2825-114 Monte de Caparica, Portugal; [b] Área Científica de Matemática, Instituto Superior de Engenharia, R. Conselheiro Emídio Navarro, 1949-014 Lisboa, Portugal.

Publicado em: *Journal of Vacuum, Science and Technology A 21, 2 (2003) 375-380*

An experimental study of the dependence of current intensity with pressure, at different constant voltages, $V_a \leq 450$ V, in the pressure range between 3.3 and 66.7 Pa, is made for an argon-copper planar magnetron discharge. At $V_a \leq 360$ V, the current increases with pressure, until approximately 12 Pa, where a maximum is observed and then decreases leading the discharge almost to extinction. At intermediate voltages, the relative current maximum, at approximately the same pressure, is followed by a local minimum after which a linear increase is observed. At higher voltages, the structure of maxima and minima tends to fade out. An empirical relation with two terms is proposed for the current intensity dependence on pressure and voltage. The first term suggests an electron scattering effect. The second term is linearly dependent on pressure. This empirical model is discussed and compared with a theoretical model from literature. From this analysis, the first term is interpreted as the contribution of electrons generated inside the cathode dark space, while the second term represents the contributions to the current of ions striking the target and of secondary electrons. Results indicate the occurrence of significant ionization in the cathode dark space for the pressure range from 3 to 30 Pa. For higher pressure values and $V_a > 360$ V, the cathode sheath is relatively thin and most ionization takes place outside of it. Using both models, theoretical calculations, and experimental parameters, the thickness of the dark space as a function of pressure at several discharge voltages is obtained. © *2003 American Vacuum Society*.

THE CURRENT-PRESSURE CHARACTERISTICS OF PLANAR MAGNETRON DISCHARGES IN RARE GASES.

M. L. Escrivão[a]; P. J. S. Pereira[b]; M. H. Cabral[a]; M. R. Teixeira[a]; M. J. P. Maneira[a]

[a]CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Monte de Caparica, Portugal; [b]Área Científica de Matemática, Instituto Superior de Engenharia de Lisboa, R. Conselheiro Emídio Navarro, 1949-014 Lisboa, Portugal.

Publicado em: *Livro de Resumos da Conferência International Meeting on Applied Physics, APHYS-2003, Badajoz, Espanha, Outubro de 2003*

Planar magnetron discharge is nowadays an important technique for the production of thin films of both metallic and dielectric materials. This fact increases the scientific interest about the physical mechanisms of this type of discharge. Among other kinds of experimental measurements the acquisition of current-voltage-pressure characteristics can give some information about physical processes present in the discharge beside the efficiency of the sputtering process. In spite of the efforts to model these characteristics, a complete description of its behaviour was not obtained. Recently the authors developed an empirical relation[1] that fits well to the curves giving the variation of the current intensity with pressure, at constant voltage, for a planar magnetron discharge in argon on copper. That relation can be expressed mathematically in the form:

$$I = a\,(p-p_0)^r \exp(-bp) + c\,(p-p_0), \qquad (1)$$

where r is a constant, a, b, and c are quantities varying with voltage and p_0 is the minimum pressure that maintains a stable discharge at a given voltage. The first term is a “magnetron term” which measures the electron current intensity related to ionization inside the cathode sheath and the second term is a “diode term” and measures the current intensity, at the target, due to the ions and secondary electrons.

The aim of the present work is to verify the validity of the previous relation for other discharges in different rare gases (Ne, Kr, Xe) ignited with a different cathode.

References:

1- M. L. Escrivão, P. J. S. Pereira, M. H. Cabral, M. R. Teixeira, and M. J. P. Maneira, J. Vac. Sci. Technol. A 21 (2), 375, 2003.

DISCRETE NONLINEAR SCHRÖDINGER OPERATOR AND PIECE-WISE AREA-PRESERVING MAPS

Cristina Januário[a]; J. Sousa Ramos[b]

[a]Área Científica de Matemática, Instituto Superior de Engenharia, R. Conselheiro Emídio Navarro 1, 1949-014 Lisboa, Portugal; [b]Departamento de Matemática, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

Palestra em: *XIV International Congress on Mathematical Physics, Lisbon, July 28 – August 2, 2003.*

We study a family of piece-wise area-preserving maps of the plane $\mathbb{R}^2$ associated to the discrete nonlinear Schrödinger equation with an antisymmetric step function potential. To understand the dynamics of these maps we study the dynamics of the circle map and we compute topological invariants.

Tilings Described By Iterated Maps

J. Leonel Rocha[(a)]; J. Sousa Ramos[(b)]

[(a)] Área Científica de Matemática, Instituto Superior de Engenharia, R. Conselheiro Emídio Navarro 1, 1949-014 Lisboa, Portugal.

[(b)] Departamento de Matemática, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

Publicado em: *International Journal of Bifurcation and Chaos, 13, 7 (2003), 1923-1935.*

We construct auto-similar tilings of the plane with the same expansion coefficient, a complex Perron number, from free group endomorphisms characterized by a class of matrices with the same complex Perron eigenvalue. We define a relation between the interior and the board of the tiles and obtain some results about topological invariants of the tilings.

ON ITERATED MAPS OF THE INTERVAL WITH HOLES

J. Leonel Rocha(a); J. Sousa Ramos(b)

(a) Área Científica de Matemática, Instituto Superior de Engenharia, R. Conselheiro Emídio Navarro 1, 1949-014 Lisboa, Portugal.

(b) Departamento de Matemática, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

Publicado em: *Journal of Difference Equations and Applications 9 (3/4) (2003), 319-335.*

A kneading theory is generalized to maps of the interval with several discontinuity points and holes. Alternative methods to evaluate the topological entropy are introduced and related. Also we study the parameterization of families of maps with holes and the monotonicity properties of the topological entropy.

COMPUTING HAUSDORFF DIMENSIONS AND ESCAPE RATES

J. Leonel Rocha(a); J. Sousa Ramos(b)

(a) Área Científica de Matemática, Instituto Superior de Engenharia, R. Conselheiro Emídio Navarro 1, 1949-014 Lisboa, Portugal.

(b) Departamento de Matemática, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

Palestra em: *Dynamical Systems Conference – Denton 2003, University of North Texas, USA, 25-29 Maio de 2003.*

We consider extensions of the kneading theory of Milnor and Thurston to present a weighted kneading theory, introducing weights in the formal power series. We show that this method allows us to derive techniques to compute explicitly topological entropies, Hausdorff dimensions and escape rates.

WEIGHTED KNEADING THEORY FOR MAPS WITH HOLES

J. Leonel Rocha(a); J. Sousa Ramos(b)

(a) Área Científica de Matemática, Instituto Superior de Engenharia, R. Conselheiro Emídio Navarro 1, 1949-014 Lisboa, Portugal.

(b) Departamento de Matemática, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

Palestra em: *Mini-Workshop on Discrete Dynamical Systems: Triangular Maps, IST, 14 Fevereiro de 2003.*

The purpose of this work is to present a weighted kneading theory for unidimensional maps with holes. We introduce a weighted matrix that describes a subshift on the points of the border of the intervals on the Markov partition and also encodes the existence of discontinuity points and turning points between each point of the border and its image. Thus, using the weighted kneading determinant, we compute explicitly some topological and metrical invariants.

TÍTULO MEMÓRIA NOS RETORNOS E VOLATILIDADES DE SÉRIES FINANCEIRAS PORTUGUESAS

Autores Alda Carvalho[1] e Nuno Crato[2]

Filiações: [1]Centro de Matemática, ISEL, Lisboa, Portugal E-mail: acarvalho@dem.isel.ipl.pt; [2]CEMAPRE, ISEG, Lisboa, Portugal E-mail: ncrato@iseg.utl.pt

Publicado em: Actas do XI Congresso Anual da Sociedade Portuguesa de Estatística

Nos mercados financeiros, as séries temporais de retornos não têm memória ou têm uma estrutura com fraca memória. Os economistas admitem que o mercado está tão mais perto da eficiência quanto menor memória existir nessas séries. No entanto, as séries de volatilidades associadas costumam apresentar uma memória forte. Neste trabalho, analisamos a estrutura de retornos e de volatilidades de séries financeiras portuguesas e estimamos medidas da sua memória. Finalmente, discutimos a possibilidade de existência de memória longa e vemos como as diversas estatísticas evoluíram ao longo do tempo.

TÍTULO MEMÓRIA NOS RETORNOS E VOLATILIDADES DE SÉRIES FINANCEIRAS PORTUGUESAS

Autores ALDA CARVALHO[1] E NUNO CRATO[2]

Filiações: [1]Centro de Matemática, ISEL, Lisboa, Portugal E-mail: acarvalho@dem.isel.ipl.pt; [2]CEMAPRE, ISEG, Lisboa, Portugal E-mail: ncrato@iseg.utl.pt

Publicado em: Actas da 7ª Conferência do CEMAPRE

Nos mercados financeiros, as séries temporais de retornos não têm memória, ou têm uma estrutura com fraca memória. Os economistas admitem que o mercado está tão mais perto da eficiência quanto menor memória existir nessas séries de retornos. No entanto, as séries de volatilidades associadas costumam apresentar uma memória forte. Neste trabalho, analisamos a estrutura de retornos e de volatilidades de séries financeiras portuguesas e estimamos medidas da sua memória. Finalmente, discutimos a aplicabilidade de modelos de volatilidade estocástica com memória longa (LMSV).

TÍTULO INNER PRODUCT NETWORKS

Autores Gonçalo Xufre Silva[1] e António José Rodrigues[2]

Filiações: [1]Centro de Matemática, ISEL, Lisboa, Portugal E-mail: goncaloo@dem.isel.ipl.pt; [2]Centro de Investigação, FCUL, Lisboa, Portugal E-mail: ajrodrigues@fc.ul.pt

Publicado em: Proccedings of. Soft Computing and Complex Systems, Coimbra, Portugal

The two types of neural networks most used for supervised learning problems are multilayer perceptrons (MLPs) and radial basis function (RBF) networks. The main difference between them is that RBFs are linear in the parameters and MLPs are not. The only way to have MLPs linear in the parameters is to impose that the weights of the connections between input and hidden units are pre-defined and fixed during all the process of training (in a three layer network). This paper describes a new type of supervised neural networks called Inner Product Networks (IPN). The model is inspired by an initialization method for the weights of a MLP proposed by Denoeux 1993. We adopt that same procedure for preprocessing the original input patterns, thus obtaining normalized ones. By using a sigmoidal activation function, we make the model relatively similar to a MLP where the nonlinear input-to-hidden weights are replaced by a subset of the input patterns. Therefore, these reference patterns have a role similar to the centres of RBFs.

IDENTIFICAÇÃO E CONTROLO DE PROCESSOS VIA INTERNET

Pedro Miguel Abreu Silva

Mestrado em: *Engenharia Mecânica*

Grau Concedido por: *IST – Universidade Técnica de Lisboa*

Orientadore: *Professor José Manuel Gutierrez Sá da Costa (IST).*

Co-Orientador: *Professor* João *Manuel Ferreira Calado (ISEL)*
Provas Concluídas em: *22 de Maio de 2003*

O grande desenvolvimento tecnológico surgido nos últimos anos tem levado a uma revolução nos métodos de ensino até hoje utilizados. Neste momento, o ensino da engenharia passa obrigatoriamente pela utilização de laboratórios e equipamentos. Apesar das vantagens introduzidas por este “novo” ensino, novos problemas surgem: número de alunos cada vez mais elevado, horários cada vez mais preenchidos, laboratórios pequenos para o número de alunos, etc. Devido a todos estes factores começam a surgir novas necessidades no ensino em geral e na área de controlo de sistemas em particular.

Desta forma apresenta-se nesta tese uma arquitectura de identificação e controlo de sistemas via Internet. Utilizando sistemas físicos presentes em laboratório, é conseguida uma ligação remota a estes via Internet, obtendo-se assim a possibilidade de proceder a testes de identificação, controlo e monitorização remotamente. Novas metodologias de controlo e identificação podem ser testadas, bem como, metodologias tradicionais podem ser utilizadas com fins educacionais, como por exemplo, controladores Proporcionais-Integrais-Derivativos, técnicas de identificação ARX, etc. Utilizando esta nova tecnologia dá-se a hipótese de utilização de um laboratório de controlo de sistemas, disponível vinte e quatro horas por dia, a toda a comunidade estudantil, bem como, a toda a comunidade científica.

ASSESSMENT OF NON-POLLUTING ANODISING PROCESSES FOR ALUMINIUM 2024 ALLOYS

J.C.S. Fernandes[a] , R. Picciochi[a], M. Da Cunha Belo[a], T. Moura e Silva[b], M.G.S. Ferreira[a,c] J.B. Ferreira[d], I.T.E. Fonseca[d]

[a]Instituto Superior Técnico, Department of Chemical Engineering, 1049-001 Lisboa, Portugal
[b]Instituto Superior de Engenharia de Lisboa, Department of Mechanical Engineering, 1950-062 Lisboa, Portugal
[c]University of Aveiro, Dept. of Ceramics and Glass Engineering, 3810-193 Aveiro, Portugal
[d]CECUL, Faculty of Sciences, University of Lisbon, 1749-016 Lisboa, Portugal

Publicado em: *Livro de Resumos do International Symposium on New Trends in Molecular Electrochemistry - XII Encontro da Sociedade Portuguesa de Electroquímica, Lisboa, 2003*

Anodising is a usual process in aeronautical industry for enhancement of anticorrosive properties of aluminium alloys. The most current processe are the chromic acid anodising (CAA) and sulphuric acid anodising (SAA). The former uses etching and anodising baths containing Cr VI, which are toxic and carcinogenic. Moreover, the environmental impact of this chemical is of growing concern and it is expected that the European Union might legislate in order to impose the abolition of such baths in a near future. Although widely used in aircraft industry, SAA is responsible for a decrease in the fatigue life of anodised aluminium, so it is not allowed in some high strength alloys used for structural parts.

The aim of this work is to show progresses reached with an alternative anodising process based in sulphuric/boric baths, under different operating conditions. Traditional processes of chromic acid anodising and sulphuric acid anodising were used as reference.

The corrosion resistance of the anodised materials was determined by electrochemical impedance spectroscopy and outdoor exposure. The present results show that a good protection is achieved with the sulphuric/boric process.

The structure of the oxide films formed on AA2024 with the different anodising processes and its dependence on the anodising and sealing parameters were investigated by scanning electron microscopy and transmission electron microscopy and compared in order to interpret their corrosion performance. The films formed on commercial aluminium using the same anodising conditions were also investigated, as a way for assessing the influence of the alloying elements.

Photoelectrochemical spectroscopy and capacitance measurements were used to assess the electronic properties of anodic oxide films formed by the different processes, in order to obtain information on the electronic structure of these films. It was found out that capacitance measurements may give valuable information on the characteristics of an anodic film, as different patterns are observed for anodised samples prepared under different conditions.

ESCOAMENTOS VISCOSOS DE FRONTEIRA LIVRE DO NÍVEL MICRO E MESOSCÓPICO DURANTE O PROCESSO DE RTM

Z. Dimitrovová [(a)]; S. G. Advani [(b)]

[(a)] IDMEC, Instituto de Engenharia Mecânica, Tel.: + 351 218 419 462, Fax: + 351 218 417 915, e-mail: zdimitro@dem.ist.utl.pt

/ .Instituto Politécnico de Lisboa, Instituto Superior de Engenharia de Lisboa, Departamento de Engenharia Mecânica, Rua Conselheiro Emídio Navarro, 1949-014 Lisboa, Portugal, e-mail: zuzana@dem.isel.ipl.pt,

[(b)] University of Delaware, Department of Mechanical Engineering, 126 Spencer Laboratory, Newark, DE 19716, Tel.: + 1 302 831 8975, Fax: + 1 302 831 3619, e-mail: advani@me.udel.edu,

Publicado em: *Acta do VII Congresso de Mecânica Aplicada e Computacional, pp. 355-364, 14-16 de Abril, 2003, Évora, Portugal*

Mostram-se neste artigo aspectos numéricos relacionados com escoamento viscoso do número de Reynolds baixo e de fronteira livre no nível micro e mesoscópico. Apresenta-se uma discussão ligada a determinação da passagem de fronteira de líquido usando o Programa de Fronteira Livre (PFL) desenvolvido com este objectivo. Os aspectos numéricos relacionados com a conservação global de massa (CGM) como o principal factor de exactidão de progressão são descritos em pormenores e uma estratégia na modelação numérica para assegurar a CGM mesmo para os números capilar baixos é sugerida. O PFL representa um trabalho de programação complexo com ligação automática de módulos escritos em Fortran, Ansys Parametric Design Language (APDL) e Maple, que são aplicados a Ansys CFD (computational fluid dynamics) módulo Flotran para resolver uma análise de base. O PFL tem todas as capacidades de capturar a formação dinâmica dos vazios ou bolhas de ar.

FAULT DETECTION APPROACH BASED ON FUZZY QUALITATIVE REASONING APPLIED TO THE DAMADICS BENCHMARK PROBLEM

J. M. F. Calado,[a] F. P. N. F. Carreira,[a] M. J. G. C. Mendes,[a] J. M. G. Sá da Costa,[b] M. Bartys,[c]

[a]Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal E-mail: {jcalado,fcarreira,mmendes}@dem.isel.ipl.pt
[b]Departamento de Engenharia Mecânica, IST, Lisboa, Portugal E-mail: sadacosta@dem.ist.utl.pt
[c]Institute of Automatic Control and Robotics, Varsóvia, Polónia E-mail: bartys@mchtr.pw.edu.pl

Publicado em: *Livro de Abstracts da SAFEPROCESS'2003, 5th IFAC Symposium on Fault Detection, Supervision and Safety of Technical Processes, Washington D.C., U.S.A., Junho 2003.*

A computer assisted fault detection methodology based on a fuzzy qualitative simulation algorithm is described. The adoption of fuzzy sets allows a more detailed description of physical variables, through an arbitrary, but finite, discretisation of the quantity space. The fuzzy representation of qualitative values is more general than ordinary interval representation, since it can represent not only the information stated by a well defined real interval but also the knowledge embedded in the soft boundaries of the interval. Such a methodology was applied to a pneumatic servomotor actuated control valve that is the benchmark problem of the EC RTN DAMADICS.

FAULT ISOLATION BASED ON HSFNN APPLIED TO DAMADICS BENCHMARK PROBLEM

J. M. F. Calado,[a] R. Louro,[b] M. J. G. C. Mendes,[a] J. M. G. Sá da Costa,[b] M. Kowal,[c]

[a]Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal E-mail: {jcalado,mmendes}@dem.isel.ipl.pt
[b]Departamento de Engenharia Mecânica, IST, Lisboa, Portugal E-mail: sadacosta@dem.ist.utl.pt
[c]Institute of Control and Computational Eng., Zielona Góra, Polónia E-mail: m.kowal@issi.uz.zgora.pl

Publicado em: *Livro de Abstracts da SAFEPROCESS'2003, 5th IFAC Symposium on Fault Detection, Supervision and Safety of Technical Processes, Washington D.C., U.S.A., Junho 2003.*

The present paper is concerned with the application of a hierarchical structure of fuzzy neural networks (HSFNN) to fault isolation on a pneumatic servo-motor actuated valve that is the benchmark considered for all the DAMADICS (Development and Application of Methods for Actuator Diagnosis in Industrial Control Systems) project partners. The adoption of a hierarchical structure of fuzzy neural networks for fault isolation purposes aims the development of an architecture that can localise abrupt and incipient single and multiple faults correctly or at least with a minimum misclassification rate and be easily trained, from only single abrupt fault symptoms.

FREE BOUNDARY VISCOUS FLOWS AT MICRO AND MESOLEVEL DURING LIQUID COMPOSITES MOLDING PROCESS

Z. Dimitrovová [a]; S. G. Advani [b]

[a] IDMEC, Instituto de Engenharia Mecânica, Tel.: + 351 218 419 462, Fax: + 351 218 417 915, e-mail: zdimitro@dem.ist.utl.pt

/ .Instituto Politécnico de Lisboa, Instituto Superior de Engenharia de Lisboa, Departamento de Engenharia Mecânica, Rua Conselheiro Emídio Navarro, 1949-014 Lisboa, Portugal, e-mail: zuzana@dem.isel.ipl.pt,

[b] University of Delaware, Department of Mechanical Engineering, 126 Spencer Laboratory, Newark, DE 19716, Tel.: + 1 302 831 8975, Fax: + 1 302 831 3619, e-mail: advani@me.udel.edu,

Publicado em: *CD de comunicações e Acta do 14th International Conference on Composites Materials, pp. 598-599, 14-18 de Julho, 2003, San Diego, California, EUA.*

Numerical simulation aspects related to low Reynolds number free boundary viscous flows at micro and mesolevel during the resin impregnation stage of the Liquid Composite Molding (LCM) Process are presented in this article. Free boundary program (FBP), developed by the authors is used to track the movement of the resin front accurately by accounting for the surface tension effects at the boundary. Issues related to the global and local mass conservation (GMC and LMC) are identified and discussed. Unsuitable conditions for LMC and consequently GMC are uncovered in mesolevel filling at low capillary number, and hence a strategy for the numerical simulation of such flows is suggested.

FBP encompasses a set of subroutines that are linked to modules in ANSYS. FBP can also capture the void formation dynamics based on the analysis developed. We present resin impregnation dynamics in two dimensions. Extension to three dimensions is a subject for further research. Several examples of stabilization validation techniques are compared.

INPUT OUTPUT LINEARIZATION OF A PILOT PRESSURE PLANT USING A DYNAMIC NEURAL NETWORK.

V. M. Becerra[a] , F. Garces[b], J. M. F. Calado[c], P. M. Silva[c].
[a]Cybernetics Department, Reading University, Reading, UK E-mail: v.m.becerra@reading.ac.uk
[b]Spyral Software Ltd, Cambridge, United Kingdom E-mail: fgarces@spyralsft.co.uk
[c]Departamento de Engenharia Química, ISEL, Portugal E-mail: vborges@deq.isel.ipl.pt

Publicado em: *Livro de Resumos da IASTED International Conference on Artificial Intelligence and Applications, Benalmádena, Espanha, Setembro de 2003.*

This paper describes a method for feedback linearization based on dynamic neural network (DNN) models. The parameters of these models can be identified to reproduce the behaviour of a dynamic system. The model is then used to compute the input-output linearization transformations. The same model is used as an open loop observer to provide state information to compute the input-output linearization. An external linear controller is used to control the input output linearized system. The method is applied to a pilot scale pressure plant.

NUMERICAL SIMULATION OF FREE BOUNDARY VISCOUS FLOWS AT ALL LENGTH SCALES OF LCM PROCESS

Z. Dimitrovová (a); S. G. Advani (b)

(a) IDMEC, Instituto de Engenharia Mecânica, Tel.: + 351 218 419 462, Fax: + 351 218 417 915,
e-mail: zdimitro@dem.ist.utl.pt.
Instituto Politécnico de Lisboa, Instituto Superior de Engenharia de Lisboa, Departamento de Engenharia Mecânica, Rua Conselheiro Emídio Navarro, 1949-014 Lisboa, Portugal,
e-mail: zuzana@dem.isel.ipl.pt,

(b) University of Delaware, Department of Mechanical Engineering, 126 Spencer Laboratory, Newark, DE 19716, Tel.: + 1 302 831 8975, Fax: + 1 302 831 3619, e-mail: advani@me.udel.edu,

Publicado em: *CD de comunicações do 3th International Conference on Computational & Experimental Engineering and Sciences, 24-29 de Julho, 2003, Corfu, Grécia*

Numerical simulation aspects related to low Reynolds number free boundary viscous flows at micro, meso and macrolevel during the resin impregnation stage of the Liquid Composite Molding (LCM) Process are studied. Free boundary program (FBP), developed by the authors is used to track the movement of the resin front accurately by accounting for the surface tension effects at the boundary. FBP encompasses a set of subroutines that are linked to modules in ANSYS and has full capability of capturing the void formation dynamics. Issues related to the global and local mass conservation (GMC and LMC) are identified and discussed. Unsuitable conditions for LMC and consequently GMC are uncovered at low capillary number. Detailed discussion is devoted to the kinematic free boundary condition and progression of the free boundary according to the frontal velocities. Possible differences related to the free boundary patterns of such cases are shown.

ON THE IMPEDANCE PARAMETER SELECTION FOR ROBOT FORCE CONTROL.

F. M. Campos, J. M. Calado[a], L. F. Baptista[b], J. M. G. Sá da Costa [c]

[a] IDMEC/ISEL, Departamento de Engenharia Mecânica, Lisboa, Portugal.
E-mail: {fcampos, jcalado}@dem.isel.ipl.pt
[b] Departamento de Engenharia Marítima, ENIDH, Lisboa, Portugal.
E-mail: luisbaptista@enautica.pt
[c] Departamento de Engenharia Mecanica, IST, Lisboa, Portugal.
E-mail: sadacosta@dem.ist.utl.pt

Publicado em: *Livro de resumos da 11th International Conference on Advanced Robotics, Coimbra, Portugal, 2003.*

This paper reports the application of impedance force control on a Puma 562 robot, focusing on the impedance parameter selection. The purpose of this study is to contribute to a better understanding of the role of each impedance parameter in the force control performance. Also, some guidelines on how to select the parameters in order to achieve accurate force tracking are presented. The drawbacks of a well known type of implementation are addressed and a procedure to attenuate these limitations is tested. The presented approach was successfully implemented on a six-degree-of-freedom PUMA industrial robot controlled by a PC-based control system.

PHOTOELECTROCHEMICAL AND CAPACITANCE STUDIES ON ALUMINIUM OXIDE FILMS

R. Picciochi[a], J.C.S. Fernandes[a], M. Da Cunha Belo[a], T. Moura e Silva[b], M.G.S. Ferreira[a,c], J.B. Ferreira[d], I.T.E. Fonseca[d]

[a]Dept. of Chemical Engineering, Instituto Superior Técnico,1049-001 Lisboa, Portugal
[b]Dept. of Mechanical Engineering, Instituto Superior Engenharia de Lisboa, 1950-062 Lisboa, Portugal
[c]Dept. of Ceramics and Glass Engineering, University of Aveiro, 3810-193 Aveiro, Portugal
[d]CECUL, Faculty of Sciences, University of Lisbon, 1749-016 Lisboa, Portugal

Publicado em: *Livro de Resumos do 8th International Symposium on Electrochemical Methods in Corrosion Research - EMCR 2003, Ysermonde, 2003*

Corrosion protection of metals and alloys is often achieved by the formation of passive oxide films, which usually exhibit semiconductive properties. The resistance of the metal to corrosive attack has been found to depend upon the solid-state characteristics of the oxide film. In this frame, photoelectrochemical spectroscopy and capacitance measurements (Mott-Schottky approach) have been successfully used in the past as in-situ techniques for the characterization of passive films formed on different metals.

Although Al_2O_3 has been usually reported in the literature as an insulator, with a bandgap ranging from 8 to 9 eV, recent studies of the oxide films formed on aluminium seem to indicate that they show n-type semiconducting properties, with optical transitions ranging between 2.8 and 4.5 eV. The relationship between the solid-state properties of Al oxide films and its corrosion resistance has been studied through different approaches. McCafferty reported a dependence of the pitting potential on the flatband potential and the isoelectric point of the oxide. Similar results were presented by Menezes et al, who found out that E_{fb} increases with the tendency of Al to undergo pitting. On the other hand, Di Quarto has related the photoresponse with the different structure of the surface passive layers.

On this basis, the above-mentioned techniques were used in this work to assess the electronic properties of the oxide films formed on pure aluminium and 2024-T3 aluminium alloy under different conditions.The results obtained confirm that the oxide films formed on aluminium show a semiconductive behaviour, with bandgap energies that are identical for the oxides studied, despite their different characteristics. Moreover, from the capacitance measurements performed on commercial aluminium it is possible to ascribe an n-type semiconductive behaviour, in accordance to the literature.

It was found out that capacitance measurements may be used as a valuable technique for the assessment of the quality of anodised layers, allowing the distinction between an efficient and an inefficient sealing. Therefore, they may be used to predict the corrosion resistance of these materials.

PRODUÇÃO E GESTÃO DE DOCUMENTAÇÃO TÉCNICA

Travassos, J. M. C.[a]; Vieitas, J. A. M.[b]
[a]Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal. E-mail: joaot@dem.isel.ipl.pt
[b]Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal. E-mail: jvieitas@dem.isel.ipl.pt

Publicado em: *Anais da conferência, (p. 1025 a 1030) do VI Congresso Ibero-Americano de Engenharia Mecânica, CIBEM-6. Universidade de Coimbra, 15-18 de Outubro de 2003.*

O projecto mecânico engloba um vasto conjunto de actividades, e, no caso concreto da Engenharia Mecânica, incide na Engenharia do Produto e na Engenharia do Processo Industrial tendendo progressivamente para a Engenharia Simultânea mas tendo sempre como expressão final um conjunto de documentação técnica, que irá ser determinante na produção de equipamentos.

A actividade da Engenharia do Produto, é caracterizada pelo esforço necessário em obter protótipos que reproduzam completamente a documentação técnica e depois fazer com que estes satisfaçam o plano de inspecção e ensaios previamente definido.

À Engenharia do Processo Industrial cabe definir e elaborar desenhos de operações de fabrico, de controlo e de movimentação, bem como desenhos de dispositivos de sujeição, ferramentas específicas e calibres, além da definição de programas, procedimentos e/ou preparação de trabalho necessária para assegurar a produção.

A Engenharia Simultânea pode ser entendida como uma abordagem sistemática para integrar o desenvolvimento do produto e do processo, incorporando os valores de trabalho em equipa, tais como cooperação, confiança e partilha, de tal forma que a tomada de decisões ocorre de modo cooperativo, ao longo do ciclo de desenvolvimento. A documentação técnica está assim em íntima ligação com o projecto mecânico, tendo as técnicas de representação evoluído muito rapidamente com a massificação das tecnologias de informação, pelo que a documentação em papel e deslocação de pessoas são substituídas por comunicação a distância em tempo real, permitindo uma informação interactiva que favorece a concepção e seus desafios criativos.

A visualização espacial, a transmissão de formas e as características funcionais dos conjuntos são qualificações imprescindíveis na actividade dos engenheiros mecânicos de hoje.

A engenharia de processo desenvolver-se-á desde a obtenção das peças fundidas, passando pela maquinação, acabamento superficial e controlo.

Pretende-se com este artigo mostrar o que o ISEL, na área de Produção de Documentação Técnica, tem para oferecer aos seus alunos e à indústria, nomeadamente, o que é possível fazer e quais as limitações detectadas, utilizando tecnologias de ponta em CAD/CAE.

PROJECTO E SIMULAÇÃO NUMÉRICA DE ESTRUTURAS COMPÓSITAS COMPLEXAS

Afonso Leite, João Travassos, Zuzana Dimitrovová
Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal

Publicado em: *Actas do VII Congresso de Mecânica Aplicada e Computacional, Évora, Portugal, Abril de 2003.*

Este trabalho tem por objectivo apresentar um estudo paramétrico detalhado do comportamento estático de uma estrutura. Esta estrutura complexa, é composta de materiais compósitos reforçados por fibras e de materiais metálicos. Vantagens e desvantagens de dois modelos de elementos finitos diferentes, usados na simulação numérica realizada com o código de MEF, ANSYS, são discutidas em detalhe. Os resultados numéricos são verificados experimentalmente por extensómetros. O estudo paramétrico pormenorizado explora a ANSYS Parametric Design Language (APDL).

A optimização da estrutura deve ter origem na determinação da carga máxima que provoque a primeira falha. Com este propósito, diferentes tipos de falhas possíveis devem ser tidos em conta. Pode ocorrer desde delaminação ou falha da lâmina nos componentes compósitos, a falha na coesão ou adesão numa interface; instabilidade de alguma parte compósita exposta a altas cargas de compressão e ainda deve ser considerada a possibilidade de cedência das partes metálicas. De qualquer forma, na determinação da carga máxima correspondente à primeira falha possível, pode ser usada uma análise linear. Porém, o objectivo principal deste estudo é escolher e estabelecer exigências no modelo de elementos finitos para simulação numérica, fornecendo resultados de elevada confiança para os casos de carga estática e consequentemente ser usado para o caso de carga dinâmica por impacto.

Este trabalho contribui também para a apresentação de uma análise de sensibilidade dos resultados às propriedades constitutivas e detalhes geométricos, que é a base principal dos estudos requeridos em análises modernas. Mostra-se que a análise de sensibilidade pode ser feita através do estudo paramétrico automatizado pela APDL.

REENGINEERING AN EMBEDDED LABORATORY ALLOWING REMOTE EXPERIMENTS THROUGH INTERNET.

J. M. F. Calado[a], P. M. Silva[a] , J.M.G. Sá da Costa[b], V. M. Becerra[c].
[a]Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal E-mail: {jcalado,psilva}@dem.isel.ipl.pt
[b]Departamento de Engenharia Mecânica, IST, Lisboa, Portugal E-mail: sadacosta@dem.ist.utl.pt
[c]Cybernetics Department, Reading University, Reading, UK E-mail: v.m.becerra@reading.ac.uk

Publicado em: *Livro de Resumos do 6th IFAC Symposium on Advances in Control Education, Oulu, Finlândia, Junho de 2003.*

The paper presents a methodology for reengineering existing control systems labs allowing remote experiments through the Internet. Such a methodology is based on standard software tools applied to develop and implement a computer gateway. All the devices used in the control system lab considered in the current approach, such as sensors, actuators and controllers, as well as the computer gateway, are connected to a PROFIBUS network. The system implemented allows real-time experiments being performed remotely and could be a powerful way of studying new identification, control or fault detection and isolation algorithms independently the place where the methods are implemented.

REPARAÇÃO DE MATERIAIS COMPÓSITOS SUJEITOS A IMPACTO BALÍSTICO

Travassos, J. M. C.
Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal. E-mail: joaot@dem.isel.ipl.pt

Publicado em: *3º Congresso Luso-Moçambicano de Engenharia, Maputo, Agosto de 2003*

Este trabalho representa um esforço de transferência de tecnologia desenvolvido pela Secção de Projecto Mecânico do Instituto Superior de Engenharia de Lisboa, com vista ao desenvolvimento da investigação e do ensino na área de materiais compósitos, com especial incidência na reparação de estruturas sujeitas a impacto balístico. Neste domínio validou-se previamente o método de Vinson-Zukas descrito na bibliografia para calcular a energia absorvida pelos materiais compósitos em estudo.

A tese de mestrado em que se baseia este trabalho, orientada conjuntamente com a Universidade do Porto, obrigou ao relacionamento com outras instituições para apoio ao nível tecnológico e científico.

O estudo dos materiais compósitos estabelece uma ligação à elevada tecnologia utilizada para inovar no âmbito da produção de equipamento móvel e na investigação que lhe está subjacente; estes materiais, hoje em dia cada vez mais aplicados na indústria, carecem de técnicas expeditas para a sua permanente caracterização e desenvolvimento das suas propriedades.

SIMULAÇÃO DE IMPACTO BALÍSTICO

M. A. Severo, L. Rodrigues, P. Caldeira, J. Travassos
Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal E-mail: joaot@dem.isel.pt

Publicado em: *Livro de Resumos das 3as Jornadas Politécnicas de Engenharia, Coimbra, Portugal, Novembro de 2003.*

A presente simulação consiste na utilização de programas correntes de cálculo não linear recorrendo à técnica dos elementos finitos, AUTODYN e LS-DYNA, após a modelação clássica com as equações de Thor, para um projéctil de 9mm de diâmetro em cobre com forma semelhante a uma munição real e um alvo de alumínio com 15mm de espessura; avaliaram-se as previsões com estes programas, reproduzindo as variações de velocidade do projéctil na perfuração das placas, para as velocidades de impacto de 200, 350, 500 e 600 m/s.

Para reproduzir o impacto do projéctil com um alvo em material compósito de matriz epoxídica reforçada com fibras aramídicas utilizou-se apenas o programa AUTODYN. Para este segundo objectivo aplicou-se o mesmo modelo geométrico de alvo alterando o material para compósito em tecido de fibras aramídicas com uma sequência de empilhamento de 45º/-45º e mantiveram-se as propriedades para o projéctil. Para o alvo em material compósito foram simuladas velocidades de impacto de 600, 750 e 900m/s.

“Hydrocodes” são programas de cálculo não linear recorrendo à técnica dos elementos finitos que podem ser utilizados para simular eventos de elevada dinâmica, particularmente aqueles onde se verifica a propagação de ondas de choque. O Autodyn e o LS-Dyna são dois dos vários “hydrocodes” que existem para atingir os objectivos deste estudo. É prática corrente na utilização destes programas fazer uma revisão na definição dos materiais, equação de estado e de resposta ou reacção constitutiva, incluindo falha e respectivos modos.

Os resultados obtidos para materiais metálicos, apresentam coerência satisfatória. Espera-se numa próxima publicação melhorar estes resultados através de modelações aperfeiçoadas com ambos os programas e a devida validação experimental.

UTILIZAÇÃO DE COMBUSTÍVEIS ALTERNATIVOS NUMA FROTA DE VIATURAS PESADAS DE RSU'S

Teixeira, F.(a), Carvalho, I. S.(a), Figueiredo, J.(b)
[a]Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal E-mail: icarvalho@dem.isel.ipl.pt
[b]APVGN – Associação Portuguesa do Veículo a Gás Natural

Publicado em: *Livro de Resumos e CD-Rom das 2as Jornadas Politécnicas de Engenharia Mecânica, Automóvel, Gestão Industrial, Energia e Ambiente, Coimbra, Portugal, Novembro de 2003.*

O presente artigo tem como objectivo o estudo da viabilidade de utilização de uma alternativa ao combustível fóssil tradicional, numa grande frota de viaturas pesadas. A análise é efectuada a partir da caracterização das 201 viaturas de recolha de resíduos sólidos dos municípios que integram a Valorsul. A selecção da alternativa mais adequada é realizada com base no enquadramento da problemática em termos ambientais e energéticos, e na análise crítica às várias soluções tecnológicas disponíveis. São realizados levantamentos relativos à tecnologia, condições de exploração e opções existentes no mercado para a implementação da solução alternativa, em comparação com a situação existente. O presente estudo é de carácter aplicado, dentro dos princípios de racionalidade económica e energética e da rentabilidade na exploração, da solução preconizada à frota em questão.

De entre os principais combustíveis alternativos, selecciona-se o que apresenta melhor viabilidade de aplicação no imediato à frota em questão, garantindo reais vantagens ambientais. Procede-se então à construção de cenários, com base em pressupostos razoáveis, nos quais se compara, em termos económicos, a implementação da alternativa preconizada com a utilização de viaturas a gasóleo. O objectivo é compreender em que condições a utilização do combustível alternativo se poderá revelar economicamente vantajosa.

Para o horizonte considerado, e desde que se venham a confirmar as considerações efectuadas, a alteração da frota de RSU para viaturas a gás natural pode começar a tornar-se economicamente compensadora, num curto espaço de três ou quatro anos, desde que o custo energético do gás natural não seja superior a 50% do custo energético do gasóleo.

Comunicações científicas

ANALYTICAL AND ELECTROCHEMICAL ASSESSMENT OF THE COMPOSITION AND CORROSION RESISTANCE OF ALUMINIUM SUBSTRATES TREATED WITH BIS-[TRIETHOXYSILYLPROPYL]TETRASULFIDE (BTESPT).

A. Cabral,[a] M. F. Montemor,[b] M. G. S. Ferreira,[c]
[c]Department of Chemical Engineering, ISEL, Lisboa, Portugal
[b]Department of Chemical Engineering, Instituto Superior Técnico, Lisboa, Portugal
[a]Department of Ceramics and Glass Engineering, University of Aveiro, Aveiro, Portugal

Publicado em: *10th European Conference on Applications of Surface and Interface Analysis, ECASIA'03, Berlim October 2003*

In recent years the efforts in the search of alternative materials for chromate conversion coatings has been increasing because the environmental and healthy problems that are associated to the use of chromate ions. It was reported that silane treatments of metals could increase their corrosion performance before and after painting, if non-organofunctional silanes are used [1].
In this work, the influence of treatment time on the composition and corrosion behaviour of Bis-[Triethoxysilypropyl]Tetrasulfide on aluminium based substrates was studied. Analytical characterisation of the silane films was performed by AES/XPS and corrosion assessment was carried out by EIS and SKP. Atomic force microscopy associated with Kelvin Probe was also used to characterise the surface films. The results show that the silane film formed on AA2024 T3 subtrates seems to be thicker and more uniform than the same film formed on Al 1050 substrates. The treatment time has no significant influence on the composition and performance of the films. The silane films showed an interesting corrosion behaviour, which is comparable to the commercially used chromate treatments.

"EXPERIMENTE" ANTES DE FAZER

Manuel Matos[1)], Fernando Teixeira[1)], Margarida Portugal[2)], João Martins[1)], Helena Paulo[1)], Sérgio Costa[1)]
[1)] Instituto Superior de Engenharia de Lisboa
[2)] Grupo ESSA (Estudos Sociológicos de Sala de Aula), Faculdade de Ciências da Universidade de Lisboa

Publicado em: *Livro de Resumos do III Encontro da Divisão de Ensino da Química da SPQ, Porto, Lisboa, Portugal, Novembro de 2003. Apresentado em comunicação oral.*

No ensino das técnicas de análise química são cada vez mais complexos e sofisticados os procedimentos e equipamentos usados. Também o número de alunos em cada aula tem vindo a aumentar nos últimos anos.
Desta forma os professores são confrontados com o enorme desafio de ensinar diferentes técnicas de análise em escassas horas e, por outro lado, os alunos terão não só de aprender a técnica proposta, bem como o modo de funcionamento dos equipamentos envolvidos.
Por mais objectivos que sejam os protocolos ou técnicas fornecidos, e por mais documentação que se possa fornecer, nada resolverá o problema do reduzido tempo

de que os alunos dispõem para adaptação ao trabalho a realizar. Note-se que numa situação real, aquele processo analítico, que se pretende que os alunos realizem à primeira tentativa, é feito depois de alguns ensaios prévios e de bastante treino com os equipamentos.

Uma subjugação do processo de aprendizagem de uma nova técnica às dificuldades de operação do equipamento, afastará os alunos do essencial: a compreensão científica do método que estão a aprender.

Para obviar as dificuldades enunciadas, entre elas o curto tempo de contacto dos alunos com o equipamento, criou-se um ambiente virtual que simula a experiência que os alunos vão encontrar no laboratório. O aluno poderá experimentar ou ensaiar o protocolo experimental antes de o realizar focando a sua atenção nos aspectos conceptuais. Para tal disponibiliza-se via WWW e de acesso não restrito (as páginas podem ser consultadas de qualquer PC e a qualquer hora) folhas de hipertexto desenvolvidas usando ferramentas de software, por exemplo em *flash* e *javascript*.

Incorporando suportes visuais do equipamento, como sejam vídeos e fotografias, os alunos poderão acompanhar o desenrolar dos ensaios, através de folhas de resultados interactivas, "quadros de giz" virtuais com tutoriais e som. Com estas ferramentas o aluno encontra-se perante uma laboratório virtual idêntico ao que irá encontrar no laboratório. Poderá executar virtualmente a experiência a realizar antes de esta acontecer.

Com a introdução destes protocolos experimentais em suporte multimedia, aproximou-se o aluno da realidade que irá encontrar no laboratório tornando-se o ensino experimental bastante mais acessível, apelativo e efectivo nos de conteúdos apreendidos.

SELF-ASSEMBLY SURFACE MODIFIED INDIUM-TIN OXIDE ANODES FOR SINGLE-LAYER LIGHT-EMITTING DIODES

Jorge Morgado[1], Nunzio Barbagallo[1], Ana Charas[1,2], Manuel Matos[1,3], Luís Alcácer[1] and Franco Cacialli[4]

1) Instituto de Telecomunicações, IST, Avenida Rovisco Pais, 1049-001 Lisboa,
Dep. Eng. Química, Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal
2) Departamento de Química, Instituto Tecnológico e Nuclear, P-2686-953 Sacavém, Portugal
3) Dep. Eng. Química, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro-1, 1950-062 Lisboa
4) Department of Physics and Astronomy. University College London, Gower Street, London, WCIE 6BT, UK

Publicado em: *J. Phys. D: Appl. Phys.* 36 **(2003) 434-438**

We study the effect of indium-tin oxide surface modification by self assembling of highly polar molecules on the performance of single-layer light-emitting diodes (LEDs) fabricated with polyfluorene blends and aluminum cathodes. We find that the efficiency and light-output of such LEDs is comparable to, and sometimes better than, the values obtained for LEDs incorporating a hole injection layer of poly(3,4-ethylenedioxythiophene) doped with polystyrene sulphonic acid. This effect is attributed to the dipole-induced work function modification of indium-tin oxide.

BINDING STUDIES AND GUEST UPTAKE OF PHENOLIC POLLUTANTS BY POLYMER-BOUND CALIX[4]ARENES

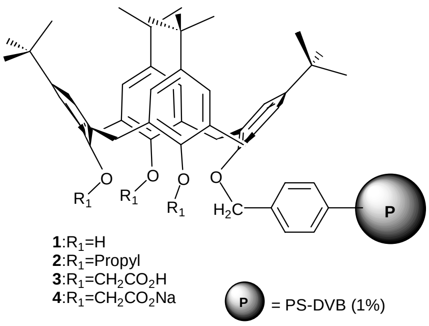
Patrícia D. Barata and José V. Prata

Secção de Química Orgânica, Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, R. Conselheiro Emídio Navarro, 1, 1949-014, Lisboa, Portugal E-mail: jvprata@deq.isel.ipl.pt

Publicado em: *Livro de Resumos do 3º Encontro Nacional de Química Analítica, Porto, Portugal, Novembro de 2003.*

The study of host-guest interactions having a calixarene molecule as a receptor is a current topic in supramolecular chemistry. The capacity of formation of inclusion complexes with aliphatic and aromatic guests is well known and has been largely demonstrated in the solid state. In solution, the sequestration studies has been performed mainly with water-soluble calix[4-8]arenes, having on occasion been shown the capacity of complex formation with organic molecules [1].

The synthesis of calixarenes covalently bound to polymeric supports has experienced a considerable development in the last few years, owing to the potential application of these polymers as ion-selective electrodes and membranes, chemical and biochemical sensors and selective extraction devices of ions [2].



Recently we have succeeded in the preparation of several new polymeric materials containing hydrophobic and hydrophilic lower rim derivatives of *p-tert*-butylcalix[4]arenes (1-4), which were envisaged as active supports in the solid-phase extraction of molecular and biomolecular species and as phase-transfer catalysts [3].

In this communication, we will present the results concerning the binding abilities and guest uptake capacities of these polymer-supported calixarenes toward pollutant phenols found in aquatic environments, obtained through batch extraction experiments. The molecular recognition efficacy of the polymer-bound calixarenes used in this work will be tentatively addressed through a comparative study undertaken with similarly functionalised PS-DVB resins in the absence of the pendant macrocyclic.

INFLUÊNCIA DO EXCESSO DE CS NA FORMAÇÃO E REDUTIBILIDADE DE NANO-PARTICULAS DE PT EM CATALISADORES BÁSICOS PT/CSB

E.R. Silva [a], C. Caldeira [a], J.M. Silva [b], M.F. Ribeiro [a], F. Ramôa Ribeiro [a]
[a]Departamento de Engenharia Química, Instituto Superior Técnico, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Livro de Resumos do 6º Encontro de Catálise e Matérias Porosos, Divisão de Catálise da Sociedade Portuguesa de Química, Évora, Portugal, Maio de 2003.*

Introdução

Estudos recentes mostraram que em sistemas zeolíticos do tipo Pt/Mβ permutados com catiões como o Na, K, Rb, e Cs existe um efeito particular da alcalinidade que contribui para o aumento da dispersão platina[1]. No caso do catião Cs é possível obter partículas de Pt muito bem dispersas e com elevada estabilidade o permite obter catalisadores com excelentes características para a aromatização de n-alcanos (n-C_6 e n-C_7). No entanto, as razões desta estabilidade e a natureza das interacções entre as espécies ainda não está esclarecida, existindo muitas questões por resolver.

Foi objectivo deste trabalho o estudo do efeito de adições crescentes de Cs na estabilização da platina em sistemas de Pt/Csβ e a influência na sua redutibilidade. Estudou-se ainda o efeito do teor de Pt na actividade, selectividade e estabilidade catalítica dos zeólitos preparados.

Parte Experimental

Para a preparação dos catalisadores partiu-se do zeólitos HTEAβ fornecido por RIPP. O zeólito foi previamente calcinado a 550ºC sob ar, sendo permutado em meio aquoso com uma solução de $CsCH_3COO$, com o intuito de obter Csβ com uma razão molar próxima de 1. O sólido, após centrifugação e secagem, foi calcinado sob ar a 500ºC durante 2 horas.

A introdução da Pt realizou-se por permuta iónica com uma solução de $Pt(NH_3)_4Cl_2$, com uma concentração tal que permitisse a introdução de 1% ou 3% de Pt em massa. Após a permuta, as amostras foram lavadas com água destilada ou com uma solução diluída de CsOH. Para eliminar o percursor de Pt as amostras foram calcinadas sob ar a 300ºC durante 2 horas.

Para obter zeólitos com diferentes quantidades de Cs recorreu-se a impregnações em meio aquoso com soluções de CsOH que continham teores de Cs que permitiram obter um excesso de Cs de aproximadamente 0,3 expresso pela razão molar de Cs/Al. Esta adição de excesso de Cs foi realizada antes da adição da Pt para umas amostras e depois para outras.

Os zeólitos obtidos foram caracterizados por análise química, redução a temperatura programada com hidrogénio (TPR) e adsorção de ciclohexano em regime dinâmico.

O comportamento catalítico foi avaliado na reacção de transformação do n-C6 utilizando um reactor tubular à pressão atmosférica e à temperatura de 450ºC. Os efluentes do reactor foram analisados por cromatografia em fase gasosa recorrendo a uma coluna capilar PONA e um detector FID.

Resultados e Discussão

Nas análises de TPR observou-se a existência de duas zonas de redução da Pt, a primeira a temperaturas entre os 100 e os 250ºC e a segunda para temperaturas compreendidas entre os 250 e os 500ºC. A primeira zona é atribuída à redução de Pt^{2+} e a segunda zona possivelmente à redução de partículas de Pt que eventualmente estejam mais retidas na estrutura zeolítica. O aumento do teor de Cs contribui para que o primeiro pico se apresente a temperaturas ligeiramente mais altas e, simultaneamente, o segundo pico diminui de intensidade.

Os ensaios de adsorção de ciclohexano permitiram verificar que à medida que o teor de Cs aumenta o volume disponível para adsorver moléculas orgânicas diminui.

Na reacção de transformação do n-C_6 ocorreu a reacção de deshidrociclização com a formação de benzeno, acompanhada de algumas reacções secundárias de isomerização (2-metil-pentano, 3-metil-pentano e 2,3-dimetil-butano), cracking (C_1-C_5) e hidrociclização (metil-ciclopentano).

Os ensaios catalíticos permitiram observar que as amostras de catalisadores com excesso de Cs que apresentavam picos de TPR intensos a 200ºC são as que têm maior selectividade para a aromatização, indicativo de uma melhor dispersão das partículas de Pt, embora se tenha verificado uma ligeira diminuição da actividade. Observou-se também que o aumento do teor de Pt contribui para o aumento da actividade e selectividade para a aromatização.

Em todos os catalisadores observou-se que a actividade decresce ao longo do tempo de funcionamento, revelando que ocorre desactivação por formação de coque[2]. Contudo o nível de desactivação observado é influenciado pela presença de um excesso de Cs. Este excesso favorece a estabilização das partículas de Pt contribuindo para uma menor desactivação. Este resultado é independente do teor de Pt do catalisador.

UTILIZAÇÃO DE MATERIAIS MESOPOROSOS COMO CATALISADORES BIFUNCIONAIS. APLICAÇÃO À ISOMERIZAÇÃO DE ALCANOS LINEARES

A. Martins [a], J. Blanchard[b], J.M. Silva [a], M.F. Ribeiro [c], F. Ramôa Ribeiro [c]
[a]Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[b]Laboratoire de Réactivité de Surface, Université Pierre et Marie Curie, França
[c]Departamento de Engenharia Química, Instituto Superior Técnico, Lisboa, Portugal

Publicado em: *Livro de Resumos do 6º Encontro de Catálise e Matérias Porosos, Divisão de Catálise da Sociedade Portuguesa de Química, Évora, Portugal, Maio de 2003.*

A preparação de peneiros moleculares siliciosos por modelação de cristais líquidos deu origem a uma nova família de materiais genericamente chamados de M41S. Estes materiais possuem canais largos cujas dimensões estão compreendidas entre 15 e 100 Å, ordenados de forma hexagonal, cúbica ou laminar, dando origem a estruturas distintas, com áreas específicas da ordem dos 700 $m^2.g^{-1}$. O membro mais importante desta família designa-se por MCM-41 e apresenta uma estrutura regular hexagonal. Mais recentemente surgiu uma outra estrutura também hexagonal designada por SBA-15.

O sucesso alcançado na preparação de materiais mesoporosos à base de sílica foi o ponto de partida para o uso do mesmo conceito para a produção de materiais com potencial para aplicações em catálise. No entanto, e uma vez que a superfície destes materiais é fracamente acídica, o passo seguinte foi o de produzir paredes porosas de sílica alumina, criando assim centros ácidos de Brönsted e propriedades de troca iónica[1].

Neste estudo procedeu-se à síntese dos materiais MCM-41 e SBA-15 na forma siliciosa. Com o objectivo de aumentar a acidez destes materiais foi feita a introdução de alumínio após a síntese da estrutura, de acordo com o procedimento descrito por Mokaya e Jones[2]. Finalmente, e com o objectivo de obter um catalisador bi-funcional, fez-se a introdução de cerca de 1% (em peso) de platina na estrutura por troca iónica. Foram assim obtidas as amostras PtAl/MCM-41, PtAl/SBA-15. Para efeitos comparativos foi usada uma sílica alumina (SiO_2-Al_2O_3 – Grace Division 13% Al_2O_3) onde foi também introduzido 1% de platina .

Foi avaliada a cristalinidade da estrutura por difracção de raios-X e determinada a área específica através de isotérmicas de adsorção/desadsorção de azoto a -196ºC.

As propriedades ácidas dos materiais foram estudadas recorrendo à adsorção de piridina seguida por Espectroscopia de Infravermelho e a caracterização da platina foi feita por Redução a Temperatura Programada com hidrogénio.

O comportamento catalítico foi estudado através da transformação do n-hexano à temperatura de 350ºC. A reacção decorreu em reactor de leito fixo, à pressão atmosférica. As amostras já calcinadas foram reduzidas *in situ* sob fluxo de H_2 ($6\ L.h^{-1}.g^{-1}$) a 500 ºC ($5ºC.min^{-1}$) durante 3 horas. A mistura reaccional consistiu numa mistura de hidrogénio e n-hexano de razão molar igual a 9 e a velocidade espacial manteve-se constante e igual a $13.2\ h^{-1}$. Os produtos de reacção foram separados e identificados por cromatografia gasosa, usando uma coluna capilar tipo SQUALANE e um detector de ionização de chama.

Os resultados obtidos por difracção de raios-X permitem concluir que as amostras mantêm a sua estrutura cristalina hexagonal típica após os tratamentos de aluminação pós-síntese e introdução de platina por permuta iónica, apesar de se observar uma ligeira redução da cristalinidade.

Os espectros de Infravermelho relativos à adsorção de piridina nos centros ácidos das amostras revelam uma acidez fraca, maioritariamente do tipo Lewis, embora também se tenha detectado a presença de centros de Brönsted com origem durante o processo de aluminação, por inserção de Al nas posições tetraédricas da rede estrutural[3].

Na caracterização da platina por Redução a Temperatura Programada observou-se um perfil de redução idêntico para todos os catalisadores, caracterizado por um pico em redor dos 200ºC e outro por volta dos 375ºC.

Durante os ensaios catalíticos obtiveram-se produtos leves (C_1 a C_5), isómeros mono-ramificados (2 e 3-metilpentano) isómeros bi-ramificados (2,2 e 2,3-dimetilbutano), metilciclopentano e benzeno.

A presença de produtos de hidrogenólise C_1 e C_5 bem como as quantidades significativas de metilciclopentano e isómeros mono-ramificados em todas as amostras, a par com uma quantidade muito pequena de produtos bi-ramificados, sugere que as reacções catalíticas ocorrem predominantemente nos centros metálicos.

A formação apreciável de benzeno comprova a baixa acidez destes materiais, mas, por outro lado revela a presença de partículas de Pt bem dispersas no suporte mesoporoso[4].

ETAT DU PT DANS LES ZEOLITHES NA-BEA ET CS-BEA EN PRESENCE DE CLUSTERS BASIQUES CS2O :CARACTERISATIONS IN SITU ET REACTIVITE CATALYTIQUE

K. Fajerwerg [a], E. Ribeiro Silva [b], L. Stievano [a], M. F. Ribeiro [b], J. M. Silva [c], P. Massiani [a]

[a] Laboratoire de Réactivité de Surface, Université Pierre et Marie Curie, UMR 7609, Paris, França

[b]Departamento de Engenharia Química, Instituto Superior Técnico, Lisboa, Portugal
[c] Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Livro de Resumos do Congresso Zéolithe Catalyse 2003, DIVCAT-GECAT-GFZ, 12 au 15 mai 2003 à Autrans, Vercors, France.*

Contexte et objectif :
De nombreux catalyseurs hétérogènes font intervenir les métaux supportés. Parmi les supports disponibles, les zéolithes présentent l'avantage de contenir des micropores qui favorisent la dispersion des particules métalliques au sein même du matériau. En outre, leur structure cristalline ainsi que leur caractère acido-basique peut être modifié, conférant ainsi au métal des propriétés électronique et catalytiques qui varient selon les interactions métal-support mises en jeu. Notre étude des systèmes Pt/BEA échangés par différents cations alcalins (Na, K, Rb, Cs) montre qu'un effet particulier de la basicité est d'augmenter la dispersion du Pt.
La basicité des zéolithes peut aussi être accrue en dispersant dans leur porosité des clusters d'oxydes de Cs, connus pour leur fort caractère basique. L'objectif de ce travail est de montrer comment des ajouts croissants de Cs dans des zéolithes Na-BEA et Cs-BEA modifient les propriétés des espèces platiniques supportées (suivi in-situ par TPO, TPR et XAS) et leur réactivité catalytique dans la conversion du n-hexane (présence de différents sites actifs).
Résultats expérimentaux
Matériaux utilisés – Deux zéolithes initiales Na-BEA et Cs-BEA (rapport Si/Al=13) ont été soumises à des imprégnations à humidité naissante avec des solutions de CsOH ou $CsCH_3COOH$ contenant des teneurs croissantes en Cs. Les échantillons ont été séchés et/ou calcinés puis le platine a été introduit sous forme de cation $Pt(NH_3)_4^{2+}$ par échange cationique en solution.
Caractérisations in situ – La dispersion de Cs_2O dans les zéolithes Na-BEA et Cs-BEA provoque i) une diminution de la température décomposition des ligands NH_3 (analyse TPO suivie par spectrométrie de masse), ii) une augmentation de l'état d'oxydation du Pt (analyse EXFAS in situ au seuil LIII du Pt) et iii) une modification de la réductibilité des espèces après calcination (TPR suivie par catharométrie et XAS in situ). Le degré d'oxydation important du Pt associé à un pic de réduction intense vers 230°C lorsque le rapport atomique Csexcès/Alréseau atteint 0,4 suggèrent une forte interaction des cations Pt^{2+} avec les clusters Cs_2O. Une conséquence notable de cette interaction métal-support est l'accroissement de la dispersion métallique après réduction.
Catalyse – Les différents échantillons ont été testés dans la conversion du n-hexane. Nous montrerons que les modifications de sélectivité observées sont corrélées aux caractéristiques des différents sites actifs présents sur les échantillons (homogénéité et taille des particules métalliques, effets électroniques, sites acides résiduels).

SURFACE PHOTOCHEMISTRY: A NOVEL LASER-INDUCED LUMINESCENCE RESULTING FROM BENZOPHENONE WHEN INCLUDED INTO *O*-PROPYLATED *P-TERT*-BUTYLCALIX[4]ARENES

Margarida R. Vieira Ferreira,[b] Luís F. Vieira Ferreira,[a] José P. Da Silva,[a,c] Isabel Ferreira Machado,[a] Anabela S. Oliveira,[a] José V. Prata[b]
[a]Centro de Química-Física Molecular - Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[b]Secção de Química Orgânica, DEQ, Instituto Superior de Engenharia de Lisboa, R. Conselheiro Emídio Navarro, 1950-062 Lisboa, Portugal
[c]FCT, Universidade do Algarve, Campus de Gambelas, 8000 Faro, Portugal

Publicado em: *Livro de Resumos do 2nd Mediterranean Meeting on Photochemistry, Giardini Naxos, Italy, 28th June-2nd July 2003.*

Time resolved laser induced luminescence (LIL), diffuse reflectance laser flash-photolysis (DRLFP) and ground-state diffuse reflectance absorption spectroscopy are relatively new techniques that can be applied to study opaque and crystalline systems.[1,2] These solid state photochemical methods have been applied by our group to study several organic compounds adsorbed onto different hosts such as *p-tert*-butylcalix[n]arenes (CLX[n], n=4, 6 and 8).[3]

The ability of calixarenes and calixarene derivatives to form inclusion complexes, accommodating guest molecules in their intramolecular cavities, greatly depends on the size and geometry of guest molecule but also on the host cavity.[3,4] In this communication we present a DRLFP and LIL study of solid powdered samples of benzophenone (BZP) included into CLX[4] and *O*-propylated *p-tert*-butylcalix[4]arenes (PrCLX[4]). Experimental evidence will be presented here, showing the occurrence of a photochemical reaction of BZP and PrCLX[4].

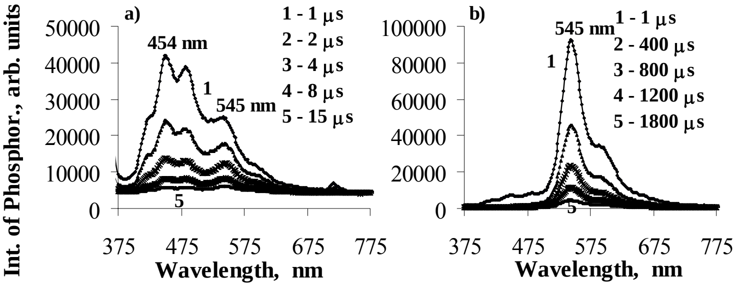


Figure 1: Laser induced room temperature phosphorescence emission spectra from air equilibrated samples of BZP/tri-*O*-propyl-p-*tert*-butylcalix[4]arene inclusion complex (molar ratio 1:2.5). a) 500 ns gate width. b) 20 ms gate width.

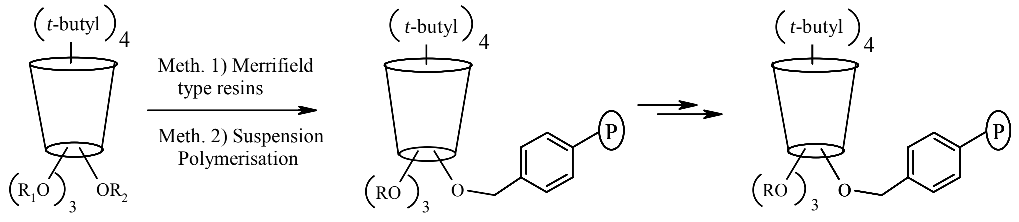
SYNTHESIS OF POLYMER-BOUND CALIX[4]ARENES

Patrícia D. Barata, Alexandra I. Costa, Paulo A. Granja and José V. Prata
Secção de Química Orgânica, Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, R. Conselheiro Emídio Navarro, 1, 1949-014, Lisboa, Portugal E-mail: jvprata@deq.isel.pt

Publicado em: *Livro de Resumos do 5º Encontro Nacional de Química Orgânica-1º Simpósio Luso-Japonês, Aveiro, Portugal, Julho de 2003.*

Calixarenes are a versatile class of synthetic cyclic oligomers that possess intramolecular bow-shaped cavities capable of accommodate guest molecules or ions. Such host properties have been explored in several contexts, ranging from reaction catalysis to molecular recognition. In particular, the syntheses of polymeric materials incorporating calixarene units on the polymer backbone or the anchoring of appropriate functionalised calixarenes onto an insoluble or soluble polymeric matrix are recent developing areas of the chemistry of such compounds.

The work described in this communication deal with the synthesis of polymeric materials containing lower rim derivatives of the *p-tert*-butylcalix[4]arene (**1**), capable of use as molecular receptors in a wide scope of applications. The adequated choice of the substituents present in the lower rim permitted the development of two synthetic ways to the target polymers. One was the attachment, *via* hydroxyl group, of a trifunctionalised calix[4]arene derivative (**2**) to a Merrifield type resin and the other was the use of a tetrafunctionalised calix[4]arene (**3**) possessing one appropriated vinyl arm, apt to be used as a *co*-monomer in suspension polymerisations with styrene. The direct immobilisation of the unsubstituted tetrahydroxycalix[4]arene (**1**) onto the polymer support was also attempted despite of the predictable enhance degree of cross-linking introduced. Further synthetic elaboration on the polymers thus obtained allowed the preparation of several useful derivatives (**7**).



1: $R_1=R_2=$ H
2: $R_1=$ Propyl or COPh; $R_2=$H
3: $R_1=$ Propyl or COPh; $R_2=CH_2PhCHCH_2$

4: R=H (method 1, from **1**)
5: R= Propyl or COPh (Meth.1, from **2**)
6: R= Propyl or COPh (Meth.2, from **3**)

7: R=H, R=CH_2CO_2Et, R= CH_2CO_2H

Acknowledgements. We thank Instituto Politécnico de Lisboa (Portugal) for partial financial support (project IPL/15/2001) and for a research fellowship to one of us (P.A.G.).

POTENTIAL ALTERNATIVES TO Cr VI-BASED PRE-TREATMENTS ON ALUMINIUM AND GALVANISED STEEL

A.C. Bastos[a], R.G. Duarte[a], A. Cabral[b], M.F. Montemor[a], A.M. Simões[a] and M.G.S. Ferreira[c]*
[a]Department of Chemical Engineering, Instituto Superior Técnico, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[c]Department of Ceramics and Glass Engineering, University of Aveiro, Aveiro, Portugal
mgferreira@cv.ua.pt

Publicado em: *Livro de Resumos do 54th Annual Meeting of the International Society of Electrochemistry, S. Pedro, Brasil, 31 Agosto a 5 de Setembro (2003).*

Cr-VI based pre-treatments have been in use for long time on several materials, namely on aluminium alloys and galvanised steels. As it is known health and environmental problems make them a target of great criticism and forthcoming legislation could definitely ban them.

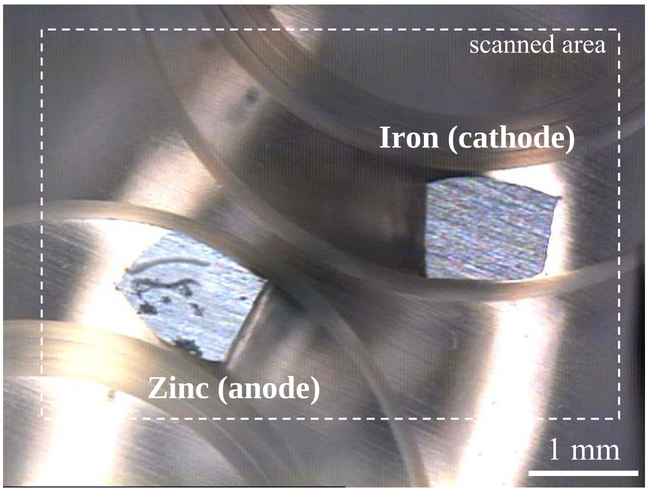
Different Cr-free alternatives have been reported, based on non-toxic or low toxicity chemicals, aiming to obtain processes that confer to the treated surfaces corrosion resistance, adherence to organic coatings and fatigue resistance identical to those obtained with chromates. Reliability and quality control are also important aspects to have in mind. However, when this set of key properties is considered, none of the substitutes could be considered, so far, performing identically to chromates.

In spite of the above, some of the alternative processes show high potential, if some improvements are carried out and the mechanisms involved are better understood.

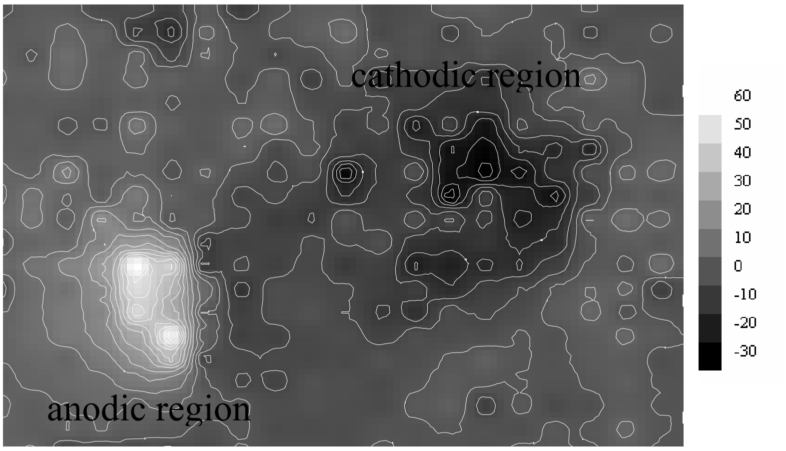
In the present work first the main groups of alternative methods that could be used for pre-treatments of aluminium and its alloys as well as of galvanised steel are revised, indicating their pros and cons. Then the study focus on the use of organosilanes, zirconium and rare earth (Ce, La) salts, showing the role of the surface films obtained with these compounds on the corrosion resistance of the substrate. A comparison is made with chromate, where studies were also carried out. The techniques used were d.c. polarisation, electrochemical impedance spectroscopy (EIS), SEM, atomic force microscopy associated with Kelvin probe, SVET and Auger/XPS spectroscopy. On painted specimens salt spray was carried out.

The results allow discussing how certain species or films formed affect the rate of cathodic and anodic reactions, i.e., the mechanism involved in hindering corrosion.

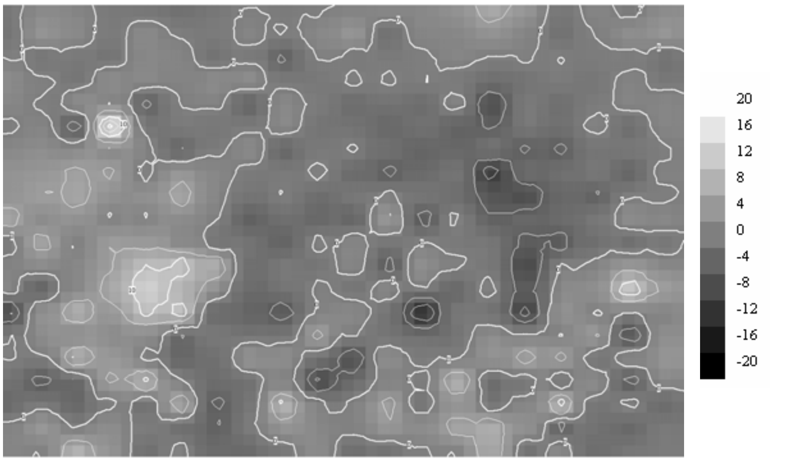
Keywords: Cr-free pre-treatments, chromate conversion, aluminium, galvanised steel, Kelvin probe, SVET



a)



b)



SVET maps showing the current densities (μA.cm^{-2}) of an iron-zinc galvanic couple in contact with 0.1 NaCl solution (a) for 18 hours and (b) 20 min after addition of chromate to the previous solution. By the presence of chromate ions, not only the anodic area on zinc was suppressed, but mainly the cathodic area on iron. Thus, chromate seems to have also an important role in inhibiting the cathodic reaction.

THE POTENTIAL OF SILANES AND RARE EARTH SALTS FOR CHROMATE REPLACEMENT ON ALUMINIUM ALLOYS AND GALVANIZED STEEL

M.G.S. Ferreira[a], R. Duarte[b], A. Cabral[c], M.F. Montemor[b], A.M. Simões[b]
[a]Department of Ceramics and Glass Engineering, University of Aveiro, Aveiro, Portugal
[b]Department of Chemical Engineering, Instituto Superior Técnico, Lisboa, Portugal
[c]Department of Chemical Engineering, ISEL, Lisboa, Portugal

Publicado em: *Livro de Resumos do EMCR'03 - 8th International Symposium on Electrochemical Methods in Corrosion Research, May 4-9, 2003, Ysermonde, Belgium*

Cr-VI based pre-treatments have been in use for long time on several materials, namely on aluminum alloys and galvanized steels. As it is known health and environmental problems make them a target of great criticism and in the near future they could be definitely banned.

Different Cr-free alternatives have been reported, based on non-toxic or low toxicity chemicals, but none of them could be considered performing identically to chromates. Every treatment shows pros and cons when sets of key properties are considered. These include effectiveness for preventing corrosion and adhesion promotion for organic coatings, fatigue resistance, reliability and quality control.

In spite of the above a certain number of alternatives show high potential, if some improvements are carried out and the mechanisms involved are more deeply understood.

The present work focus on the use of silanes (BTESPT and APS) and rare earth (Ce, La) salts as chromate substitutes for Al 2024 aluminum alloy and galvanized steel. These compounds when applied by immersion and subsequent curing originate films that improve corrosion resistance and paint adherence to organic coatings. The films formed are characterized by Kelvin probe, SVRET, AFM, SEM and Auger/XPS. Corrosion resistance was assessed by electrochemical impedance spectroscopy, d.c. polarization and salt spray.

Comparison with the chromate conversion is also carried out, simultaneously with the discussion of the mechanisms involved in the different processes.

Keywords: Cr-free pre-treatments, Silanes, Kelvin probe, SVET, AFM, SEM, XPS, chromate conversion, aluminium, galvanised steel, BTESPT, APS, Auger

---

THE POTENTIAL OF SILANES AND RARE EARTH SALTS FOR CHROMATE REPLACEMENT ON ALUMINIUM ALLOYS AND GALVANIZED STEEL

M.G.S. Ferreira[a], R. Duarte[b], A. Cabral[c], M.F. Montemor[b], A.M. Simões[b]
[a]Department of Ceramics and Glass Engineering, University of Aveiro, Aveiro, Portugal
[b]Department of Chemical Engineering, Instituto Superior Técnico, Lisboa, Portugal
[c]Department of Chemical Engineering, ISEL, Lisboa, Portugal

Publicado em: *Livro de Resumos do V LATINCORR 2003, 5º Congresso de Corrosion de la NACE Region Latinoamérica / 8º Congresso Iberoamericano de Corrosion e Proteccion, 20 a 24 de Outubro, Santiago, Chile (2003)*

Cr-VI based pre-treatments have been in use for long time on several materials, namely on aluminum alloys and galvanized steels. As it is known health and environmental problems make them a target of great criticism and in the near future they could be definitely banned.Different Cr-free alternatives have been reported, based on non-toxic or low toxicity chemicals, but none of them could be considered performing identically to chromates. Every treatment shows pros and cons when sets of key properties are considered. These include effectiveness for preventing corrosion and adhesion promotion for organic coatings, fatigue resistance, reliability and quality control.In spite of the above a certain number of alternatives show high potential, if some improvements are carried out and the mechanisms involved are more deeply understood.The present work focus on the use of silanes (BTESPT and APS) and rare earth (Ce, La) salts as chromate substitutes for Al 2024 aluminum alloy and galvanized steel. These compounds when applied by immersion and subsequent curing originate films that improve corrosion resistance and paint adherence to organic coatings. The films formed are characterized by Kelvin probe, SVRET, AFM, SEM and Auger/XPS. Corrosion resistance was assessed by electrochemical impedance spectroscopy, d.c. polarization and salt spray. Comparison with the chromate conversion is also carried out, simultaneously with the discussion of the mechanisms involved in the different processes.

“ENGENHARIA” DE SUPERFÍCIES E INTERFACES DE DÍODOS DE POLÍMERO POR ANCORAMENTO AUTO-ORGANIZADO DE MONOCAMADAS DE MOLÉCULAS ORGÂNICAS

J. Morgado[1,2], N. Barbagallo[1,2], A. Charas[1,2], M. Matos[1,3], P. Brogueira[4], L. Alcácer[1,2]
1) Instituto de Telecomunicações, IST, Avenida Rovisco Pais, 1049-001 Lisboa
2) Dep. Eng. Química, Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa
3) Dep. Eng. Química, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro-1, 1950-062 Lisboa
4) Dep. Física, Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa

Publicado em: *Livro de Resumos do 6º Encontro de Química-Física, Lisboa, Portugal, Agosto/Setembro de 2003.*

O ancoramento de moléculas orgânicas, de forma auto-organizada, sobre a superfície de materiais inorgânicos constitui uma estratégia muito eficiente para modificar quer a energia das superfícies quer a sua hidrofobicidade e, consequentemente, a interacção com outros materiais. A versatilidade química das moléculas orgânicas a usar, variando a natureza do grupo de ancoramento por ligação química à superfície

inorgânica, a polaridade das moléculas ou ainda a sua natureza hidrofóbia ou hidrofílica, permite a realização de estudos sistemáticos e, acima de tudo, a optimização das características da monocamada assim formada para aplicações específicas desses substratos modificados.

Neste estudo, estamos particularmente interessados em criar monocamadas dipolares sobre a superfície de um óxido misto de índio e estanho (ITO) depositado sobre vidro. Estes substratos de ITO sobre vidro são muito usados no fabrico de dispositivos optoelectrónicos, em particular, de díodos emissores de luz (LEDs). Partindo de um valor de cerca de 4.8 eV para a função de trabalho do ITO, este valor pode ser modificado até cerca de 0.6 eV por via deste tipo de modificação superficial.

Para a criação destas monocamadas dipolares sobre o ITO seleccionaram-se moléculas de benzeno para- dissubstituídas, do tipo $G\text{-}C_6H_4\text{-}A/D$, em que G é o grupo de ancoramento e A/D é um grupo aceitador ou doador electrónico, variando-se assim o momento dipolar das moléculas, –COCl, SO_2Cl e COOH são os grupos de ancoramento utilizados, e os grupos A/D usados são NO_2, CN, CF_3, H, OCH_3.

A regularidade da superfície de ITO modificada foi avaliada usando microscopia de força atómica. Para avaliar o efeito destas modificações sobre as características do ITO, mais concretamente sobre a sua função de trabalho, foram construídos LEDs de polímero em que estes eléctrodos de ITO modificados são usados como eléctrodos de injecção de buracos. As barreiras para a injecção de buracos no polímero a partir do ITO são, simplificadamente, determinadas pela diferença entre a função de trabalho do ITO e a energia da HOMO (tomada como o potencial de ionização) do polímero. Vários polímeros electroluminescentes e suas misturas foram usados na construção destes LEDs, procurando correlacionar as suas características optoelectrónicas com o tipo de moléculas usadas na modificação da superfície do ITO. Os resultados obtidos mostram uma excelente correlação entre o momento dipolar das moléculas e as características dos LEDs, nomeadamente, a corrente que circula e a tensão à qual se inicia a emissão de luz.

APPLICATION OF FOURIER-TRANSFORM INFRARED SPECTROSCOPY FOR MONITORING SEVERAL AMIDASE REACTIONS

R. Pacheco[1,2], A. Karmali [1], M.L.M. Serralheiro[2] and P.I. Haris [3]

[1] Instituto Superior de Engenharia de Lisboa, Laboratório de Engenharia Bioquímica do Departamento de Engenharia Química, Rua Conselheiro Emídio Navarro,1, 1949-014 Lisboa, Portugal

[2] Faculdade de Ciências da Universidade de Lisboa, Centro de Estudos Bioquímicos e Fisiológicos da Faculdade de Ciências da Universidade de Lisboa, Campo Grande, Edifício C8, 1749-016 Lisboa, Portugal

[3]DeMontfort University, Department of Biological Sciences, The Gateway, Leicester, LE1 9BH, United Kingdom

Publicado em: *Livro de Resumos de Second International Conference on Biomedical Spectroscopy, London, United Kingdom, July 2003.*

The aliphatic amidase (acylamide amidohydrolase, EC 3.5.1.4.) from *Pseudomonas aeruginosa* catalyses the hydrolysis of simple aliphatic amides[1]. This enzyme also hydrolyses short-chain aliphatic esters although the rates of these reactions are much slower than the amide hydrolysis [2]. In addition to these hydrolase reactions the enzyme can catalyse a transferase reaction of the acyl moiety of short chain amides, acids and esters to hydroxylamine[3]. A Fourier Transform Infrared Spectroscopy method has been developed for assaying the *Pseudomonas aeruginosa* native amidase, overproduced in an *Escherichia coli* strain, catalysed hydrolysis of acetamide with the advantage of performing a real time measurement of the enzymatic activity[4]. Here we report the use of the same procedure for the monitoring of the hydrolysis of other substrates such as propionamide, butiramide, benzamidine, phenilalaninamide, alaninamide, glycinamide and leucinamide in deuterium oxide and also the synthesis of several hydroxamic acids in deuterium oxide by the same enzyme. The intensity of the substrates amide I band maximum was measured as a function of time to determine the kinetics of amidase catalysed reactions. The Michaelis-Menten kinetics parameters V and K_m were determined for each substrate.

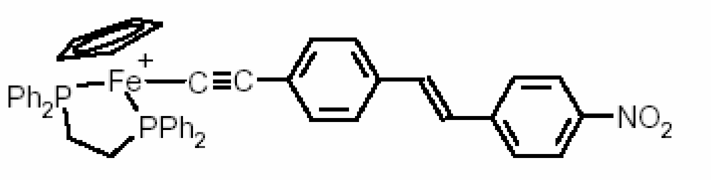
DESIGN OF ORGANOMETALLIC NITRILE AND ACETYLIDE COMPLEXES FOR SECOND-ORDER NONLINEAR OPTICS.

W. Wenseleers,[a] G. Aerts,[a] E. Goovaerts,[a] A. Bouwen,[a] M.H. Garcia,[b,c] M.P. Robalo,[b,d] A.P.S. Teixeira,[b] M.P. Cifuentes,[e] S. Hurst,[e] M.G. Humphrey[e]

[a]Physics Department, University of Antwerp (UIA), Wilrijk, Belgium.
[b] Centro de Química Estrutural, IST, Lisboa, Portugal.
[c] Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal.
[d] Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[e] Dept. of Chemistry, Australian National University, Canberra, Australia.

Publicado em: *Livro de Abstracts do 5th International Topical Conference on Optical Probes of Conjugated Polymers and Organic & Inorganic Nanostructures - Optical Probes 2003, Venice, Itália, Fevereiro de 2003.*

Organometallic complexes can be designed to have unusually strong optical nonlineari-ties[1,2]. We present a hyper-Rayleigh scattering study of a systematic series of complexes in which an organometallic donor group is incorporated in the plane of a conjugated, acceptor substituted ligand, to form push-pull chromophores. The influence of the metal (M=Co, Ni, Ru, Fe),[3] the type of linkage (M–N≡C or M-C≡C) and length and substitution of the conjugated ligand and coligand are investigated. Strategies towards the design of complexes with a suitable non-centrosymmetric crystal structure, such as the inclusion of chiral groups[3], are also discussed.



$\beta = 2315 \times 10^{-30}$ esu

SYNTHESIS AND CHARACTERISATION OF $[Fe(\eta^5\text{-}C_5H_5)(dppe)(p\text{-}NCC_6H_4NO_2)]^+$ COMPLEXES WITH DIFFERENT COUNTERIONS: GOVERNING THE CRYSTAL PACKING IN SOLID STATE?

C. Jacob,[a] M.P. Robalo,[a,b] M.H. Garcia,[a,c] M.F.M. Piedade,[a,c] M.T. Duarte,[a] A.R. Dias[a]

[a] Centro de Química Estrutural, IST, Lisboa, Portugal.
[b] Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[c] Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal.

Publicado em: *Livro de Abstracts do 7th FIGIPS Meeting in Inorganic Chemistry, Lisboa, Portugal, Junho de 2003.*

Molecular crystals, based on organic molecules or metal transition coordination complexes assembled in the solid state, as a consequence of non covalent interactions, have been the subject of important research during the last decade[1]. The interest in these materials stems from the potential to manipulate solid-state properties by systematic variations of molecular features and crystal packing motifs.

The design of organometallic materials for nonlinear optical (NLO) applications is based on two steps: maximisation of the NLO properties of the molecule modifying its structural features and optimising the crystal packing of the molecules in solid state.

From our previous work[2-4], we have identified $[Fe(\eta^5\text{-}C_5H_5)(\text{bidentate phosphine})(p\text{-}NCR)]^+$ derivatives, as promising NLO materials, the metallic centre behaving as a good electron donor group towards the coordinated nitrile and, in particular, the cationic complex $[(\eta^5\text{-}C_5H_5)(dppe)Fe(p\text{-}NCC_6H_4NO_2)]^+$ due to good stability in solution and solid state, seemed to be a good candidate for future studies.

We report herein the synthesis of organometallic complexes based on $[(\eta^5\text{-}C_5H_5)(dppe)Fe(p\text{-}NCC_6H_4NO_2)]^+$fragment and several anions (iodide, maleate, (H)maleate, fumarate, (H)fumarate, glutamate, (H)glutamate, oxamate, etc.) as assemblers, promoting the formation of hydrogen bonding networks in the solid state.These new complexes were characterised by the usual spectroscopic IR, ^1H and ^{13}C NMR techniques. X-ray diffraction studies were done in order to study the crystal packing obtained due to the introduction of the different counterions.

SYNTHESIS AND CHARACTERISATION OF ORGANOMETALLIC IRON(II) COMPLEXES WITH POTENTIAL PHOTOCHROMIC SWITCHING PROPERTIES

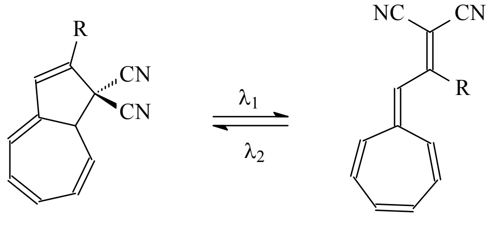
A.R. Jorge,[a] M.P. Robalo,[a,b] M.H. Garcia,[a,c] A.R. Dias[a]

[a] Centro de Química Estrutural, IST, Lisboa, Portugal.
[b] Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[c] Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal.

Publicado em: *Livro de Abstracts do 7th FIGIPS Meeting in Inorganic Chemistry, Lisboa, Portugal, Junho de 2003.*

During the last decade, light molecular switches has gained much renewed attention due to the promising applications in technological areas such as various optoelectronic devices (optical memory, photooptical switching and display), materials for nonlinear optics, etc. Although several organic photochromic molecules has been studied, photochromic systems involving transition metal complexes has been very little explored [1-3]. Nevertheless, the role of the transition metal centers has found to be relevant in the intramolecular photosensitization of the photochromic process.

This communication reports the synthesis and functionalisation of dihidroazulene type molecules, known as light molecular switches, since irradiation can be used to interconvert them reversibly between an non-conjugated (or "OFF") and a conjugated (or "ON") forms. Also the coordination of these chromophores to [Fe(η^5-C_5H_5)(dppe)] and [Fe(η^5-C_5H_5)$(CO)_2$] fragments were studied and a new family of mono and binuclear compounds was synthesised. The new complexes were characterised by the usual spectroscopic IR, ^{1}H and ^{13}C NMR techniques. Studies by UV/Vis spectroscopy were performed in order to characterise the photochromic behaviour of the new complexes.



R = $C_6H_4NO_2$, $C_6H_4N(CH_3)_2$

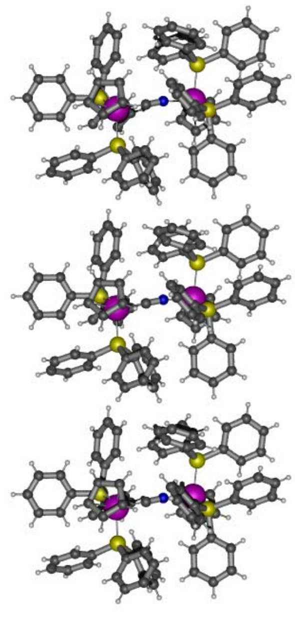
SYNTHESIS, CHARACTERISATION AND X-RAY STRUCTURE OF BIMETALLIC CYANO-BRIDGED [(η^5-C_5H_5)$(PPh_3)_2$Ru(μ-CN)Ru$(PPh_3)_2$(η^5-C_5H_5)][PF_6]

C. Ornelas,[a] C.G. Gandum,[a] J.C. Rodrigues,[a] M.H. Garcia,[b,c] N. Lopes,[b] M.P. Robalo,[b,d] A. Roulamo,[e] K. Rissanen[e]

[a] Centro de Química da Madeira, Universidade da Madeira, Funchal, Portugal.
[b] Centro de Química Estrutural, IST, Lisboa, Portugal.
[c] Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal.
[d] Departamento de Engenharia Química, ISEL, Lisboa, Portugal.
[e] Department of Chemistry, University of Jyväskylä, Jyväskylä, Finland.

Publicado em: *Livro de Abstracts do 7th FIGIPS Meeting in Inorganic Chemistry, Lisboa, Portugal, Junho de 2003.*

Although metal cyano bridged binuclear compounds have been extensively studied due to their mixed-valence charge transfer properties, the actual number of studies of their potential non-linear optical (NLO) properties, however, remains rather small[1]. Our previous work on the preparation and characterization of organometallic compounds for NLO applications[2], mainly based in the iron and ruthenium monocylopentadienyl moieties, leaded us to study the previously prepared[3] complex [(η^5-C_5H_5)$(PPh_3)_2$Ru(μ-CN)Ru)$(PPh_3)_2$(η^5-C_5H_5)]PF_6 (**1**). The title compound (**1**), was obtained unexpectedly from the reaction of a organometallic precursor [(η^5-C_5H_5)$(PPh_3)_2$RuCl] and alifatic bisnitrile. During the reaction the bis-nitrile has decomposed and formed a cyanide anion. The title molecule (**1**) crystallizes in an acebtric triclinic space group (P1) with one molecule in the unit cell (Z = 1). The molecules of (**1**) pack along the *a*-axis by van der Walls and π-π interactions forming acentric 1-D piles (figure). The orientation of the cyanide anion is near perpendicular to the direction of the 1-D piles inside which the anion resides. As the NLO properties manifest themselves in acentric or polar crystal lattices, particularly the efficiency of second harmonic generation (SHG) using the Kurtz powder method of **1** is under study. The complex (**1**) was fully characterized by ^{1}H, ^{13}C, ^{15}N, ^{31}P NMR, MS, FTIR, UV-Vis, CV and by elemental analysis.



PREPARATION OF PERCURSORS FOR THE SYNTHESIS OF NLO METALLODENDRIMERS USING RUTHENIUM(II) FRAGMENTS AND 1,3,5-TRICYANOBENZENE DERIVATIVES

C.G. Gandum,[a] J.C. Rodrigues,[a] M.H. Garcia,[b,c] N. Lopes,[b] M.P. Robalo,[b,d] H. Mansikkamäki,[e] K. Rissanen[e]

[a] Centro de Química da Madeira, Universidade da Madeira, Funchal, Portugal.
[b] Centro de Química Estrutural, IST, Lisboa, Portugal.
[c] Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal.
[d] Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[e] Department of Chemistry, University of Jyväskylä, Jyväskylä, Finland.

Publicado em: *Livro de Abstracts do XVth FECHEM Conference on Organometallic Chemistry, Zurich, Suíça, Agosto de 2003.*

Although the search for new organometallic materials displaying nonlinear optical (NLO) properties is the focus of much current research activities, the synthesis and characterization of metallodendrimers for NLO applications has been far less studied. In particular and despite metal ions such as ruthenium(II) are excellent templates for building 3D octopular NLO metallodendrimers[1], the insertion of Ru complexes fragments at specific nodes via the nitrile group is, to the best of our knowledge, unknown. The use of ligands with octupolar symmetry and a π-delocalised system, such as the acceptor 1,3,5-tricyanobenzene (TCB) or the 1,3,5-tris(p-cyanostyryl)benzene (TCSB) makes this approach particularly interesting for the synthesis of non-dipolar planar metallodendrimers with high intramolecular charge transfer. In this work we will present the most relevant spectroscopic and structural results about the preparation of ruthenium complexes linked to the octupolar molecules via the nitrile bounded groups, having in view their possible use as precursors for the preparation of metallodendrimers for NLO purposes. The compounds have been prepared using our previous experience on the synthesis of ruthenium organometallic compounds with NLO properties,[2] by a divergent synthetic process, using the TCB or TCSB as a core, with the complex fragments $RuCl(PMe_3)_4$ and $Ru(dppe)_2$ inserted in the periphery, by abstraction of one of the chlorides of the parent complexes $[Ru(PP)_2Cl_2]$ (PP = dppe, $(PMe_3)_2$). Aspects of the IR, UV-Vis, NMR spectra of the new complexes are discussed. X-ray studies of the compounds are under progress.

SYNTHESIS AND CHARACTERIZATION OF SOME HETERONUCLEAR COMPLEXES OF IRON (II)

Sílvia S. P. R. Almeida[a,b], M. Fátima Guedes da Silva[b], Lucjan Jerzykiewicz[c], Piotr Sobota[c] and Armando J.L. Pombeiro[b]

[a]Instituto Superior de Engenharia de Lisboa, Lisboa, Portugal.
[b]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Lisboa, Portugal.
[c]Faculty of Chemistry, University of Wroclaw, Wroclaw, Poland.

Publicado em: *Livro de Abstracts do 7th FIGIPS Meeting in Inorganic Chemistry, Lisboa, Portugal, Junho de 2003.*

The study of transition metal complexes with cyanide bridges is a field of growing interest, namely in Bioinorganic Chemistry since cyanide is a known substrate of nitrogenase and a ligand in active sites of Ni-Fe and Fe-only hydrogenases. Moreover, cyano-bridged complexes are of significance in electron-transfer processes and materials chemistry. Whithin our continued interest on the activation of small molecules, we have been investigating the coordination chemistry of cyanide at mononuclear Re(I) and Fe(II) phosphinic centres and found its suscepbility to undergo H-bond formation and protonation to give, in the latter case, the simplest isocyanide CNH or aminocarbyne CNH_2 ligands.

We now report the results of the extension of the activation of cyanide towards various transition metal Lewis acids-$[WCl_4(PPh_3)_2]$, $[ReOCl_3(PPh_3)_2]$, $[NiCl_2(PCY_3)_2]$, $[PdCl_2(PPh_3)_2]$ and $[PtCl(Ph)(PPh_3)_2]$ - to give heteronuclear adducts with bridged cyanide. Their syntheses and spectroscopic characterization are presented, as well as results of an X-ray diffraction analysis of a trinuclear complex with the *[Fe–C≡N–W–N≡C–Fe]* unit. The bridging and mono-hapto coordination modes of cyanide are compared.

UNEXPECTED COMPLEX DOUBLE SALT WITH POLY(PYRAZOLYL) BORATE IRON(III). CRYSTAL STRUCTURE OF $[FE(HB(PZ)_3)_2][FECL_4]$ $\{HB(PZ)_3$ = HYDROTRIS(1-PYRAZOLYL)BORATE$\}$

E. C. B. Alegria[a,b], L. M. D. R. S. Martins[a,b], T. F. S. Silva[b], M. F. C. Guedes da Silva[a,c] and A. J. L. Pombeiro[a]

[a]Centro de Química Estrutural, IST, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[c]Universidade Lusófona de Humanidades e Tecnologias, Lisboa, Portugal

Publicado em: *Livro de Abstracts do 7th FIGIPS Meeting in Inorganic Chemistry, Lisboa, Portugal, Junho de 2003.*

There is a current growth of interest in complexes containing tris(pyrazolyl)borate ligands, due to their importance in synthetic inorganic, bioinorganic and organometallic chemistries.

In pursuit of our work on the activation of small molecules with biological, environmental or synthetic significance (like nitriles or cyanamides), we have attempted the preparation of half-sandwich $HBpz_3$ iron(II) complexes with such substrates, trying to overcome the tendency of the poly(pyrazolyl)borate ligands to give full-sandwich complexes of the type $[M(HBpz_3)_2]$.

In the course of these attempts, we have obtained an unexpected complex double salt of iron(III), $[Fe(HB(pz)_3)_2][FeCl_4]$, and we now report its synthesis and characterization by IR and multinuclear NMR spectroscopies, X-ray diffraction, FAB^+-MS spectrometry, elemental analysis and electrochemical methods. Other $HBpz_3$ complexes formed in those reactions are also reported.

REACTIONS OF THE ALLENYLIDENE COMPLEX *TRANS*-$[FEBR(=C=C=CPH_2)(DEPE)_2][BPH_4]$ WITH NUCLEOPHILIC AGENTS

A. I. F. Venâncio,[§,†] M. F. C. Guedes da Silva,[§,≠] L. M. D. R. S. Martins,[§,†] and A. J. L. Pombeiro[§]

[§]Centro de Química Estrutural, IST, Lisboa, Portugal
[†]Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[≠]Universidade Lusófona de Humanidades e Tecnologias, Lisboa, Portugal

Publicado em: *Livro de Abstracts do 7th FIGIPS Meeting in Inorganic Chemistry, Lisboa, Portugal, Junho de 2003.*

In pursuit of our studies on the chemistry of allenylidene iron(II) complexes, in this work we explore some reactions of the compound *trans*-$[FeBr(=C=C=CPh_2)(depe)_2][BPh_4]$ (depe = $Et_2PCH_2CH_2PEt_2$) with a secondary and a primary amine ($NHMe_2$ and NH_2Me, respectively) and a phosphine (PMe_3), in acetonitrile. They have afforded the monocationic alkynyl compound *trans*-$[Fe(NCMe)\{-C\equiv C-CPh_2(X)\}(depe)_2][BPh_4]$ (X = NMe_2 or NHMe) and the dicationic alkynyl complexes *trans*-$[Fe(NCMe)\{-C\equiv C-CPh_2(PMe_3)\}(depe)_2]Y_2$ (Y_2 = $[BPh_4]_2$ or $[BPh_4]_{2-x}Br_x$). Their syntheses, spectroscopic and FAB-MS properties, as well as the single crystal X-ray structural analysis of the monocationic complex *trans*-$[Fe(NCMe)\{-C\equiv C-CPh_2(NMe_2)\}(depe)_2]^+$ are reported.

REACTIONS OF CYANAMIDE AT A N_2–BINDING MOLYBDENUM CENTER. FORMATION OF CYANOIMIDE SPECIES

E. C. B. Alegria[a,b], L. M. D. R. S. Martins[a,b], M. F. C. Guedes da Silva[a,c], S. M. P. R. M. Cunha[a] and A. J. L. Pombeiro[a]

[a]Centro de Química Estrutural, IST, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[c]Universidade Lusófona de Humanidades e Tecnologias, Lisboa, Portugal

Publicado em: *Livro de Abstracts do II Santa Maria Workshop on Chemistry – devoted to Bioinorganic Chemistry, University of Havana, Cuba, Julho de 2003*

The coordination chemistry of cyanamide ($N\equiv C-NH_2$) is still an underdeveloped field of research in spite of the recognized interest of this species namely as a substrate of

Mo- and V- nitrogenases and of cyanamide hydratase, with applications in agriculture and in treatment of alcoholism. There has also been a recent growth of interest in complexes containing the cyanoimide (NCN) ligand, due to their potential applications in catalysis, as precursors for metal nitrides or carbonitrides, or intermediates for organocyanamides.

We have previously obtained some cyanamide complexes of Mo, Re or Fe and now we report the reaction of the acylated complex *trans*-[Mo(NCN){NCNC(O)Et}(dppe)$_2$]Cl (dppe = $Ph_2PCH_2CH_2PPh_2$) (obtained by electrophilic attack with EtC(O)Cl to the cyanoimide ligand in *trans*-[Mo(NCN)$_2$(dppe)$_2$]) with [Et_3O][BF_4] and HBF_4 to give the unexpected *trans*-[MoCl(NCN)(dppe)$_2$][BF_4] and organic cyanamides (NCNEtC(O)Et or NCNHC(O)Et), the former characterized by IR, multinuclear NMR spectroscopies, FAB$^+$-MS spectrometry, elemental analysis, X-ray diffraction and electrochemical methods.

CATHODICALLY INDUCED REACTIONS OF SOME CYANAMIDE AND ISOCYANIDE COMPLEXES

L. M. D. R. S. Martins
Centro de Química Estrutural, IST, Lisboa, Portugal
Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Livro de Abstracts do New Trends in Molecular Electrochemistry and XII Meeting of the Portuguese Electrochemical Society, Academia das Ciências de Lisboa, Portugal, Setembro de 2003*

Cyanamide (N≡C-NH_2) and methylisocyanide (C≡NMe) are recognized substrates of nitrogenase, being the first mainly reduced to ammonia plus methylamine (six electrons) and ammonia plus methane (eight electrons) and the later to methane plus methylamine (six electrons) and dimethylamine (four electrons); their activation is believed to proceed by coordination to a transition metal present at the active centre (Mo, V or Fe). Within our interest on the activation of small molecules with biological significance, such as cyanamide or methylisocyanide, and on the understanding of their enzymatic reactions, namely those involving proton- or hydrogen-transfer, we have investigated the coordination chemistry of cyanamide or methylisocyanide at Mo- or Fe-hydride centres [MoH_4(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) and *trans*-[FeHCl(dppe)$_2$] and we found the occurrence of a cathodically-induced dehydrogenation at a cyanamide ligand at [MoH_2($NCNH_2$)(dppe)$_2$]$^{2+}$ to give a deprotonated species [MoH_2(NCNH)($NCNH_2$)(dppe)$_2$]$^{2+}$ whereas the methylisocyanide ligand at *trans*-[FeH(CNMe)(dppe)$_2$]$^+$ can undergo activation towards protonation to give dimethylamine, in a 4-electron process which possibly involves the formation of an iron(0) centre.

ELECTROCHEMICAL BEHAVIOUR OF THE CYANOIMIDE-TYPE COMPLEXES trans-[Mo(NCN){NCNC(O)R}(dppe)$_2$]Cl AND trans-[Mo(NCN)Cl(dppe)$_2$][BF_4]

E. C. B. Alegria,[a,b] S. M. P. R. M. Cunha,[a] L. M. D. R. S. Martins,[a,b] M. F. C. Guedes da Silva[a,c] and A. J. L. Pombeiro[a]
[a]Centro de Química Estrutural, IST, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

[c]Universidade Lusófona de Humanidades e Tecnologias, Lisboa, Portugal

Publicado em: *Livro de Abstracts do New Trends in Molecular Electrochemistry and XII Meeting of the Portuguese Electrochemical Society, Academia das Ciências de Lisboa, Portugal, Setembro de 2003*

Cyanamide ($NCNH_2$) is a small organonitrogen molecule with industrial, biological and scientific interest. One can emphasize, for example, its role as an alternative substrate of both Mo- and V-nitrogenases, the nitrogen fixation enzymes.

In the sequence of our interest in the coordination and activation of such substrate by transition metal centres, we have attempted the reaction of the phosphinic bis(dinitrogen) complex of Mo(0) *trans*-$[Mo(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with cyanamide. The obtained product was the unexpected bis(cyanoimide) complex of Mo(IV) *trans*-$[Mo(NCN)_2(dppe)_2]$ (**1**). In fact, cyanamide was not only coordinated but also reductively dehydrogenated by the electron-rich Mo(0) centre to the cyanoimide (NCN^{2-}) form.

In **1**, the N_β of one of the two cyanoimide ligands is susceptible of attack by acid chlorides RC(O)Cl (R = alkyl or aryl), affording the acylated and aroylated derivatives *trans*-$[Mo(NCN)\{NCNC(O)R\}(dppe)_2]Cl$ (R = alkyl, acylated compound **2a**; R = aryl, aroylated compound **2b**). Both products **2a** and **2b** lead to the formation of the new mono(cyanoimide) species *trans*-$[Mo(NCN)Cl(dppe)_2][BF_4]$ (**3**) on reaction with electrophiles.

We are now reporting the electrochemical behaviours, as studied by cyclic voltammetry and controlled potential electrolysis, in aprotic media, at a Pt electrode, of the these compounds. Such behaviours are discussed in terms of electron richness of the Mo centres and the electronic properties of the ligands.

ELECTROCHEMICAL BEHAVIOUR OF CATIONIC ALKYNYL COMPLEXES OF IRON(II) WITH THE $\{FEBR(ET_2PCH_2CH_2PET_2)_2\}^+$ CENTRE

A. I. F. Venâncio[a], L. M. D. R. S. Martins[a,b] and A. J. L. Pombeiro[a]

[a]Centro de Química Estrutural, IST, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Livro de Abstracts do New Trends in Molecular Electrochemistry and XII Meeting of the Portuguese Electrochemical Society, Academia das Ciências de Lisboa, Portugal, Setembro de 2003*

In pursuit of our studies on the reactivity of allenylidene iron(II) complexes, the electrochemical behaviour of the derived alkynyl complexes *trans*-$[Fe(NCMe)\{-C{\equiv}C-CPh_2(X)\}(depe)_2][BPh_4]$ (X = NMe_2 or NHMe, depe = $Et_2PCH_2CH_2PEt_2$) and *trans*-$[Fe(NCMe)\{-C{\equiv}C-CPh_2(PMe_3)\}(depe)_2][BPh_4]_{2-x}Br_x$, has been investigated by cyclic voltammetry (CV), in 0.2M $[NBu_4][BF_4]/CH_2Cl_2$, at a Pt-wire electrode. These monocationic and dicationic alkynyl complexes were obtained from the reaction of amines ($NHMe_2$ or NH_2Me) and a phosphine (PMe_3), respectively, with the corresponding allenylidene complex *trans*-$[FeBr(=C=C=CPh_2)(depe)_2][BPh_4]$, in acetonitrile.

The three alkynyl complexes exhibit three sucessive anodic waves between 0.50 and 1.90 V *vs.* S.C.E, being the first and the third ones due to the $Fe^{II} \rightarrow Fe^{III}$ and

Fe^{III}→Fe^{IV} oxidations, respectively, and the second one to the first oxidation of the counter-ion $[BPh_4^-]$.
Moreover, it was possible to estimate the P_L and E_L parameters for these alkynyl ligands, whose net electron-donor/acceptor character is compared with related species such as alkynes.

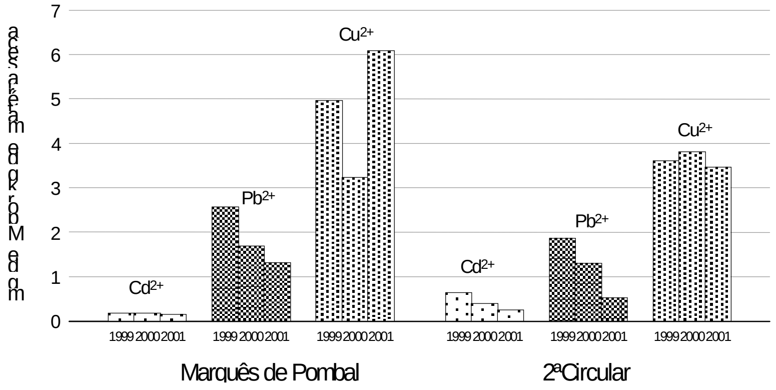
DETERMINAÇÃO DA POLUICÃO POR Pb, Cd E Cu NA CIDADE DE LISBOA

N. A. F. Silva[a] , M. J. Matos[a], Hugo Silva[a], Vasco Matos, Tiago Arruda, M. I. S. Lopes[b], R. A. E. Leitão[a]

[a]Departamento de Engenharia Química, ISEL, Lisboa, Portugal, E-mail: nsilva@deq.isel.ipl.pt
[b]Departamento de Química e Bioquímica, ISEL, FCUL, Portugal

Publicado em: *Livro de Resumos do 3º Encontro Nacional da divisão de Química Analítica da Sociedade Portuguesa de Química, Porto, Portugal, Novembro de 2003.*

O presente trabalho pretende contribuir para o desenvolvimento e implementação de métodos de análise quantitativa de metais tóxicos por serem poluentes com propriedades específicas, destacando-se a sua bioacumulação, a partir do ar, água, solos ou alimentos para consumo humano.
Neste trabalho utiliza-se como bioindicador, e desde 1999, o choupo (Populus), abundante em toda a área estudada (cidade de Lisboa). Esta é uma espécie de folha caduca, garantindo-se assim, que os teores determinados a partir das suas folhas dizem respeito apenas a um ano .A quantificação do teor em Pb, Cd e Cu nas folhas de choupo foi efectuada por Voltametria de Redissolução Anódica (SWASV), método validado por Espectrofotometria de Absorção Atómica com Câmara de Grafite (GFAAS). Apresentam-se abaixo os resultados obtidos para as zonas do Marquês de Pombal e 2ª Circular.



Observa-se que o chumbo e o cádmio apresentam uma evidente diminuição temporal enquanto o cobre apresenta uma variabilidade não sistemática. Para aferir com rigor a origem destes metais irá proceder-se à análise do solo por EDXRF. Desenvolveu-se uma estratégia de amostragem dos solos que consideramos ser a mais adequada para o ambiente urbano em que as árvores estão plantadas.

OPTIMIZAÇÃO DO MÉTODO DE SWASV PARA DETERMINAÇÃO DE Cu, Pb E Cd EM AMBIENTE URBANO

N. A. F. Silva[a] , M. I. S. Lopes[b] , R. A. E. Leitão[a] , M. J. Matos[a] , Hugo Silva[a]

[a]Departamento de Engenharia Química, ISEL, Lisboa, Portugal, E-mail: nsilva@deq.isel.ipl.pt
[b]Departamento de Química e Bioquímica, ISEL, FCUL, Portugal

Publicado em: *Livro de Resumos do 6º Encontro Nacional da divisão de Química Física da Sociedade Portuguesa de Química, Lisboa, Portugal, Agosto e Setembro de 2003.*

Nesta comunicação serão apresentados os resultados da optimização do método de voltametria de redissolução anódica (SWASV) aplicado à determinação de cobre, cádmio e chumbo em amostras reais.

Depois da quantificação dos teores destes metais na cidade de Lisboa usando folhas de choupo (populus) como bioindicador e como método de análise a absorção atómica em câmara de grafite, pretendeu-se validar um método alternativo, porventura mais rápido e económico, o SWASV, método que apresenta uma potencial vantagem adicional pela possibilidade de determinação simultânea dos três metais em estudo.

A aplicação deste método a amostras reais não é trivial dados os inúmeros factores operacionais que têm que ser optimizados para garantir análises reprodutíveis. A complexidade da matriz em que se encontra o analito é sem dúvida a principal causa da complexidade intrínseca envolvida na optimização e aplicação deste método.

Após digestão ácida por microondas, as amostras foram submetidas à aplicação do método de SWASV tendo sido optimizados os seguintes parâmetros operacionais: concentração de mercúrio, potencial de deposição do mercúrio, tempo de deposição do mercúrio, potencial de limpeza do filme de mercúrio, tempo de limpeza do filme de mercúrio após deposição, tempo de limpeza do filme de mercúrio entre medições, potencial de deposição dos metais a analisar, tempo de deposição dos metais a analisar, frequência da onda quadrada, amplitude da onda quadrada, incremento de potencial, desarejamento da solução, concentração de ácido nítrico, agitação.

Foram utilizadas amostras de folhas de choupo de dois locais da cidade de Lisboa: Marquês de Pombal e Segunda Circular recolhidas em três anos consecutivos (1999-2001).

A optimização e validação do método SWASV para este tipo de amostras permitiu que se disponha de um processo de validação dos resultados geralmente complexos associados a este tipo de análises ambientais.

DOSEAMENTO DO CÁLCIO EM MEL MONOFLORAL

M. I. Godinho, A.Catarino, N. Alua, A. R. Miranda, M. Silva, H. Silva, M. C. Serra

DEPARTAMENTO DE ENGENHARIA QUÍMICA, ISEL, LISBOA, PORTUGAL

Publicado em: *Livro de Actas do 6º Encontro de Química de Alimentos - IPIMAR, Lisboa, Junho de 2003.*

Amostras de mel de rosmaninho, trevo, incenso, eucalipto e urze provenientes de diversas regiões do país foram caracterizadas em termos de acidez e teor em cinzas. Em seguida, procedeu-se ao doseamento do cálcio nas diversas amostras através de espectrofotometria de absorção atómica com uma chama de ar/acetileno. De um modo geral, os resultados obtidos encontram-se no intervalo de valores referidos na

literatura e permitiram efectuar um estudo comparativo dos diferentes tipos de mel monofloral em relação ao teor em cinzas, pH, acidez total e concentração em cálcio

Palavras chave: Mel monofloral, Espectrofotometria de absorção atómica, Cálcio

---

SOLUBILITY OF METHANE IN WATER AND IN A MEDIUM FOR THE CULTIVATION OF METHANOTROPHS BACTERIA

Maria Celeste C. Serra, [a, b] **A.M.F. Palavra** [a]

[a]Centro de Química Estrutural, IST, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Livro de Resumos do Encontro Jorge Calado: 40 Years of Molecular Thermodynamics, Instituto Superior Técnico, Lisboa, Portugal, Janeiro de 2003.*

Solubility of gases in liquids is reported in many application areas and also has a relevant theoretical interest. In particular, the solubility of simple hydrocarbons in water provides information about hydrophobic interactions and at the same time is becoming increasingly important for engineering and environmental studies.

Although the methane-water system had been studied by others authors some years ago, it may deserves consideration today in chemical process industries and in the evaluation of water hydrocarbon pollution because the more stringent existent regulations.

The atmospheric methane is, fundamentally, produced by the decomposition of organic matter. However, most of this gas is oxidized microbiologically before it reaches the atmosphere by the methane-utilizing bacteria, which contribute for the maintenance of a low level of methane in the atmosphere. Therefore, the measurement of the methane solubility in a medium with the appropriate composition to sustain growth of these bacteria will be useful for the quantification and optimisation of the fermentation process.

In this way, the solubility of methane in water and in an aqueous medium for the cultivation of methanotrophs bacteria was determined in the temperature range 293.15 to 323.15K and at the atmospheric pressure. The measurements were carried out in a Ben-Naim/Baer type apparatus with a precision of about ± 0.3%. The experimental results were processed using rigorous thermodynamic methods and the mole fractions of the dissolved gas at the gas partial pressure of 101.325kPa, the Henry coefficients at the water vapour pressure and the Ostwald coefficients at infinite dilution were obtained.

A comparison between the solubility of methane in water and those observed in fermentation medium in the temperature range of 298.15 to 308.15K has shown that this gas is about ± 2.3% more soluble in water.

The temperature dependence of the mole fractions was also accounted using the Clarke-Glew-Weiss fitting equation and the thermodynamic quantities, Gibbs energy, enthalpy and entropy, associated with the dissolution process were calculated.

Finally, the experimental Henry coefficients of methane in water are compared with the calculated by the scaled particle theory. The Henry coefficients estimated by this model were about ± 4% lower than the experimental ones.

ELECTRICAL CONDUCTIVITY MEASUREMENTS IN PORTUGUESE MONOFLORAL HONEYS

N. Alua, A.Catarino, M. I. Godinho, M. C. Serra
Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Livro de Resumos do XII Meeting of the Portuguese Electrochemical, Society, New Trends in Molecular Electrochemistry, Academia de Ciências de Lisboa, Lisboa, Setembro de 2003.*

The evaluation of foods quality requires a continual development of analytical methods. This aspect is particularly important in the detection of substances, which may involve health hazards, such as the presence of toxic metals in foods.

An experimental program on the determination of metals in honey was implemented in the Laboratório de Controlo Analítico of ISEL. In fact, honey is used worldwide as a sweetener in a variety of foodstuffs and the studies with portuguese honeys are scarce. Therefore, it is worthwhile to perform more analytical tests for its quality evaluation.

The determination of electrical conductivity is used in routine honey control because it is good quality criteria and also a method for testing its botanical authenticity. It is a very quick and easy method and may be an indirect way of measuring the mineral content of a honey. Furthermore, recent studies reference the increase of the conductivity values with the ash and acid content.

The aim of this work is to find the correlation between the electrical conductivity and the ash content, and to discuss the possible influence of honey botanic origin.

This way, a lot of samples of portuguese monofloral honeys were collected and the electrical conductivity measurements were carried out. The experimental data are in a good agreement with other values from the literature, showing a linear relationship with the ash content determined in a previous work. Moreover, it was found that the honey botanic origin could affect the conductivity results.

AVALIAÇÃO DE PARÂMETROS FÍSICO-QUÍMICOS DE MEL MONOFLORAL

M. C. Serra, A. Catarino, N. Alua, M. Silva, M. I. Godinho
Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Livro de Resumos do 3º Encontro Nacional de Química Analítica, Analitica´03, Porto, Portugal, Novembro de 2003.*

Os actuais requisitos de segurança alimentar exigem a atribuição de critérios de qualidade, para os quais é fundamental o desenvolvimento de métodos de análise que permitam a caracterização físico-química de alimentos.

O presente trabalho enquadra-se num projecto experimental que visa a determinação de elementos metálicos em alimentos, nomeadamente em mel. Neste contexto, procedeu-se à caracterização físico-química de vários tipos de mel monofloral produzido em Portugal. Os parâmetros avaliados poderão contribuir para uma melhoria na produção e comercialização deste produto, uma vez que são indicadores da sua qualidade e origem botânica.

Deste modo, foi realizado um estudo comparativo entre sete tipos de mel monofloral de diferentes regiões do país: rosmaninho, trevo, incenso, flor de laranjeira, urze, queiró e eucalipto. Os parâmetros físico-químicos avaliados foram os seguintes: teor

em cinzas, pH, acidez total, índice de refracção, teor em água, conductividade eléctrica e rotação específica.
Os estudos efectuados permitiram estabelecer correlações entre alguns dos parâmetros analisados. De um modo geral, os resultados obtidos encontram-se no intervalo de valores determinado por outros autores para méis monoflorais produzidos em diferentes países.

SOME STRUCTURAL ASPECTS AND PURIFICATION OF RECOMBINANT AMIDASE FROM *E. coli.*

Sónia Martins [a], Amin Karmali [a], Maria Luísa Serralheiro[b]
[a]Secção de Biotecnologia, Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[b]Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal

Publicado em: *Livro de Abstracts do INTERNATIONAL SYMPOSIUM – Separation and Characterization of Natural and Synthetic Macromolecules, Amsterdam, The Netherlands , February 2003.*

Amidase (acylamide amidohydrolase EC 3.5.1.4) from *Pseudomonas aeruginosa* catalyses the hydrolysis of aliphatic amides producing the corresponding acid and ammonia.
This enzyme also catalyses the transfer of acyl groups of short-chain amides to hydroxylamine producing short-chain hydroxamic acids which are widely used as growth factors, antibiotics and tumor inhibitors.
Site-directed mutagenesis was used to isolate altered amidases which are able to produce long-chain hydroxamic acids. Hence, the amidase gene from a wild-type strain 8602 of *P. aeruginosa* was altered by site-directed mutagenesis at positions T103I(AI3), W138G, W138S, H275K-T103I, H275K, H281K and C91A and expressed in *Escherichia coli*. Several mutant strains of *P. aeruginosa* were isolated from the wild-type strain 8602. A mutant strain of *P. aeruginosa* AIU 1N (R188C) was also isolated from a AI3 strain in an acetanilide/urea medium. The constituve mutant L10 from *P. aeruginosa* has a spontaneous mutation in the amidase regulatory gene whereas a mutant strain KLAM59 (E59V) was isolated from strain L10.
The aim of this work was to investigate the enzyme activity of wild-type and mutant amidases in the presence and absence of β-mercaptoethanol and EDTA in native PAGE.

DIFFERENTIAL BEHAVIOUR OF LACCASE FROM *Fusarium sp.* ON IMMOBILIZED METAL AFFINITY CHROMATOGRAPHY

Vanda Pacheco [a], Amin Karmali [a], Pablo Pereira [b], José C. Roseiro [b]
[a]Laboratório de Engenharia Bioquímica da Secção de Biotecnologia do Departamento de Engenharia Química do Instituto Superior de Engenharia de Lisboa.
Rua Conselheiro Emídio Navarro, 1900 Lisboa.
[b]Laboratório de Microbiologia Industrial, Instituto Nacional de Engenharia e Tecnologia Industrial
Azinhaga dos Lameiros, Paços do Lumiar, Lisboa.

Publicado em: *Livro de Resumos do Hydroxyapatite Conference, Lisbon,3th – 5th November 2003*

Laccase (EC 1.10.3.2) catalyses the reduction of dioxygen to water as well as the oxidation of a wide range of phenolic and related compounds. This enzyme differs

from peroxidase because it does not require hydrogen peroxide to oxidize substrate. In fact, electrons are transferred to molecular oxygen (O_2) producing H_2O.
This enzyme plays an important role in pulp and paper industry[1,2] as well as in biodegradation of environmental pollutants such as dechlorination of chlorophenolic compounds.As far as analytical applications are concerned, laccases have been used as enzyme electrodes[3] ,in order to measure phenolic contents in aqueous samples such as wine, fruit juices and tea.
The differential behaviour of laccase from *Fusarium sp.* on immobilized metal affinity chromatography (IMAC) was investigated by using Metal (II)-iminodiacetic acid (IDA) agarose columns. The enzyme bound only to Cu(II)-IDA-agarose column since laccase did not exhibit adsorption to other metals (Ni^{2+}, Zn^{2+} and Co^{2+}) columns. The effect of pH was also investigated in the binding of the enzyme to immobilized metal chelates and laccase bound strongly as the pH increased from 6.0 to 8.0.
Laccase from *Fusarium sp.* was purified in one step by immobilized metal affinity chromatography (IMAC) on Cu (II) –IDA agarose column. The enzyme was eluted from the column with a linear gradient (0 - 30 mM) of imidazole and fractions containing enzyme activity were pooled and concentrated by pressure dialysis. Laccase was purified in one step with a recovery of enzyme activity of about 80% and a purification factor of 130 and a specific activity of 45U/mg protein.

FURTHER STUDIES ON THE STRUCTURAL CHARACTERIZATION OF THE TERNARY MIXTURE METHANOL-ACETONITRILE-1-PROPANOL.

F. Martins[a], R. Elvas Leitão[b], N. Nunes[b] , M. C. Ventura[c]
[a]CQB/Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal
[b]CQB/Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[c] CECUL/Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal

Publicado em: *Livro de Resumos do IX ESOR, Oslo, Noruega, Julho de 2003.*

Structural and dynamic studies in mixed solvents have gone through significant developments both from an experimental and from an interpretative point of view. This is inevitably linked to the foreseen applications of these solvents in fields as varied as analytical chemistry, industrial processes and the design of biological environments.
Most published works refer to binary mixtures in which complexities such as preferential solvation phenomena and synergistic effects, among others, have been detected. However, ternary mixtures, being more complex, are potentially more informative, since the variability of most of their properties can be significantly increased through adequate choice of components and compositions. Among properties that influence the physicochemical behaviour of solvents, polarity, Lewis acidity, polarizability and molecular size are some of the most prominent.
In this work we carry on with the static characterization of the referred ternary mixture and its binary counterparts[4], having determined for this purpose several solvent descriptors such as ETN, nD and Vm, at 25 ºC, for the three pure components, 22 molar fractions of the ternary mixture and 18 molar fractions of each of the binary mixtures.

REACTIVITY STUDIES OF TERTIARY ALKYL BROMIDES IN PROTIC AND APROTIC SOLVENTS: FURTHER DEVELOPMENTS

L. Moreira[a], F. Martins[a], R. Elvas Leitão[b]

[a]CQB/Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal
[b]CQB/Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Livro de Resumos do IX ESOR, Oslo, Noruega, Julho de 2003.*

Many questions regarding the reactivity of tertiary haloalkanes in liquid phase reactions remain still open to discussion. Important contributions to these issues have been achieved using LSER approaches in terms of multi-descriptor equations. However, most published material has dealt solely with the behaviour of these substrates in protic solvents and their aqueous mixtures. This has lead to limited data set spans and therefore to narrow descriptors' variation and to significant cases of inter-correlations. Moreover, limitations related to MLR itself, in particular, the use of insufficient data points, as seen, for instance, in a recent paper by Gajewski, weakens any further analysis both from a statistical and a physicochemical perspective.
These facts urged the need to obtain additional data for these reactions. In this work we report the results for the reactions of 2-bromo-2-methylpropane, 2-bromo-2-methylbutane, 3-bromo-3-methylpentane and 3-bromo-3-ethylpentane, at 25 ºC, in an appropriate number of both protic and aprotic solvents. These solvents were carefully chosen in order to ensure, on one hand, a significant enlargement of the descriptors space and, on the other, to pursue the desirable target of defining a property balanced set of solvents for a correct application of multiparametric regression analysis.

IS THERE DIFFERENTIAL SOLVATION IN THE HETEROLYSES OF 3-X-3-METILPENTANES(X=CL, BR,I) ?

L. Moreira[a], F. Martins[a], R. Elvas Leitão[b]

[a]CQB/Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal
[b]CQB/Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: Livro de Resumos do IX ESOR, Oslo, Noruega, Julho de 2003.

Tertiary alkyl halides are convenient substrates to probe solvation differences in heterolysis reactions on changing the dimension and characteristics of the leaving group. Although several studies have been performed with this purpose, some of which recently, they refer to tert-butyl halides reactions in a small set of solvents, which results in insufficient statistical confidence.It is, therefore, interesting to analyze the reactivity of other similar substrates in an adequate set of solvents both in number and diversity.
In the above context, a comparative study of the heterolyses of 3-X-3-Metilpentanes(X=Cl, Br, I) in a set of protic and aprotic solvents characterized by a

wider variation of Lewis acidity and basicity, dipolarity, polarizability and cohesion density energy has been performed, at 25.00 ºC.

This study led to the setting up of multiple Linear Solvation Energy Relationships (LSER) for the three substrates in order to: i) disclose possible differences in solvation effects, such as the decrease in anion solvation due to hydrogen bonding by protic solvents, on decreasing the density of charge of the halide ion, as predicted earlier for substrates of the same type; ii) address the issues of nucleophilic assistance as well as that of the role of the solvent's coordinate.

ESTUDO MECANÍSTICO DA REACÇÃO DO 3-Br-3-METILPENTANO EM DMSO-d^6

L. Moreira,[a] P. Robalo,[b,c] R. Elvas Leitão,[a,c] F. Martins[a]

[a]CQB/Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal

[b]Centro de Química Estrutural, IST, Lisboa, Portugal
[c]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Livro de Resumos do 5º Encontro Nacional de Química Orgânica da SPQ, Aveiro, Julho de 2003.*

Reacções de heterólise de substratos não carregados, nomeadamente halogenetos de butilo terciários, têm sido frequentemente usadas como sondas para o estudo do efeito de solvente. No entanto, a maior parte dos dados existentes na literatura dizem respeito ao comportamento destes substratos em meios próticos. Em particular, a informação disponível sobre substratos terciários bromados em solventes apróticos é escassa e refere-se, regra geral, ao primeiro membro da série, o t-BuBr [1-3]. No âmbito de um estudo mais alargado sobre relações estrutura-reactividade, envolvendo uma grande variedade de solventes, mostrou-se fundamental o esclarecimento mecanístico das reacções daqueles substratos em solventes apróticos.

O presente trabalho centra-se na análise mecanística por RMN de 1H da reacção do 3-Bromo-3-metilpentano em DMSO-d6, a 25 ºC. A reacção foi monitorizada durante dois meses, em dois tubos fechados, com concentrações de substrato distintas, 10-1 e 10-2 mol dm-3 e mantidos entre medidas sucessivas a uma temperatura de 25.0 ± 0.1 ºC. As análises por RMN de 1H da composição do meio reaccional foram efectuadas num espectrómetro Varian Unity, a 300 MHz. A informação cinética foi confirmada por via independente, recorrendo a uma técnica condutimétrica. Nos espectros obtidos a identificação das espécies produzidas na reacção foi efectuada por análise comparativa com os espectros de amostras autênticas sintetizadas. A informação recolhida e a análise dos produtos da reacção mostra-se genericamente consistente com a análise efectuada por Mitsuhashi et al.[3] para a reacção de t-BuBr em DMSO. Subsistem, no entanto, algumas dúvidas para as quais se propõem hipóteses alternativas.

APPLICATION OF QSAR TO THE MODELLING OF TUBERCULOSTATICS – PRELIMINARY STUDIES

F. Martins,[a] L. Santos, [a] R. Elvas Leitão,[b] C. Ventura[c], L. Pinheiro[d], A. Zissimos[e], M. Abraham,[e]

[a]CQB/Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal

[b]CQB/Departamento de Engenharia Química, ISEL, Lisboa, Portugal
c ISEC,/CECUL, Lisboa, Portugal
d FFUL/CECUL, Lisboa, Portugal
e Department of Chemistry, University College London, London, U.K.

Publicado em: *Livro de Resumos do XIII Congresso Nacional da Sociedade Espanhola de Química Terapêutica, Santiago de Compostela, Espanha, Setembro de 2003.*

Tuberculosis remains the leading cause of death in the world from a single infectious disease. The mechanisms of its pathogenesis, and protection from it, are complex and not entirely understood. The occurrence of resistance to either of the drugs used in multi-therapy (INH, RIF, PZA) causes major concern by leaving out only drugs far less effective and of higher toxicity. To date there is no reliable way of predicting the tuberculostatic activity of a given chemical compound.

The set up of a model equation relating appropriate physicochemical descriptors with minimum inhibitory concentrations (MIC's) for a training set of compounds previously tested in vitro, should produce relevant information regarding the design of other, potentially more active, compounds before carrying out extensive synthesis and microbiological assays. This procedure may lead to significant scale economies of effort, time and expenditure.

For this purpose we have gathered data on over 400 compounds from several known families of tuberculostatics. From these, a training and a test set have been defined in order to apply the Abraham's model equation, so that convenient structural modifications leading to activity enhancement could be inferred..

REACTIVITY STUDIES OF 2-BROMO-2-METHYLPROPANE IN BINARY MIXTURES OF PROTIC AND APROTIC SOLVENTS. CORRELATIONS WITH SOLVENT STRUCTURE

N. Nunes,[a,b] R. Elvas Leitão,[a,b] F. Martins[b],
[a]Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[b]CQB/ Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal

Publicado em: *Livro de Resumos do 28th ICSC, Debrecen, Hungria, Agosto de 2003.*

Due to the increased application of mixed solvents in fields as varied as chemistry, life sciences, industrial processes and environmental protection, structural and dynamic studies in these type of solvents have gone through significant developments in the last years.

In the sequence of recent work on the structural characterization of binary and ternary mixtures of protic and aprotic solvents1, and in the line of our interest to enlarge the matrix of substrates and solvents used, so that a reliable application of multivariate data analysis can be performed2, we have been studying the kinetics of some halogenated substrates on mixed solvents.

In this work, we report rate constants for the reaction of 2-bromo-2-methylpropane in the mixtures MeOH/1-PrOH and MeOH/MeCN, for several molar fractions, at 25.00 ºC, obtained by a conductimetric technique.

Correlation analysis between rate constants and solvent descriptors, previously determined by us, allowed the identification of the prominent solute-solvent-solvent

interaction mechanisms in the rate processes. Further reactivity and mechanistic studies are under way.

ENTALPIAS DE SOLUÇÃO DE 1-BROMOADAMANTANO EM SOLVENTES HIDROXÍLICOS A 298.15 K

N. Nunes,[ab] L. Moita,[b] R. Elvas Leitão,[ab] F. Martins[b]

[a]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

[b] CQB/Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal

Publicado em: *Livro de Resumos do 6º Encontro de Química-Física da SPQ, Lisboa, Portugal, Agosto de 2003.*

Estudos recentes têm mostrado que os compostos de adamantano e seus derivados possuem actividade antibacteriana e antiviral promissora[1]. A utilização de novos compostos com vista à sua utilização na indústria farmacêutica, deve ser sempre acompanhada por uma caracterização físico-química adequada. A calorimetria de solução é uma técnica poderosa para esse efeito, uma vez que constitui uma excelente ferramenta para a identificação de mecanismos de interacção soluto-solvente-solvente.

Nos últimos anos têm sido apresentadas pelo grupo de calorimetria do DQB/FCUL entalpias de solução de 2-X-2-metilpropano, 2-X-2-metilbutano (com X=Cl e Br) e 3-Cloro-3-metilpentano em vários solventes hidroxílicos [2-3]. Os excelentes resultados obtidos com um calorímetro de solução/reacção artesanal, mostraram que o número e posição dos grupos hidroxilo e o comprimento e ramificação da cadeia carbonada do álcool, bem como o tamanho do grupo alquilo do soluto, influenciavam invariavelmente os valores das entalpias de solução.

Neste trabalho, apresentam-se novos valores de entalpias de solução a diluição infinita para um derivado do adamantano, o 1-bromoadamantano, a 298.15 K em 13 solventes hidroxílicos, obtidos com um calorímetro de solução de precisão, da marca Thermometric, sucessor do calorímetro de solução clássico LKB 8700. Este calorímetro semi-adiabático e com várias funções computorizadas, está associado a uma unidade TAM ligada a um banho de água com uma estabilidade, em condições optimizadas, de ± 0.0001 ºC e apresenta uma resolução na temperatura da ordem do μK, correspondente a uma resolução nos valores de entalpia de 1-4 mJ, para um vaso reaccional de 100 mL. O calorímetro foi previamente testado para a reacção do TRIS quer com ácido clorídrico 0.10 M quer com hidróxido de sódio 0.05M. Para cada solvente foram realizados pelo menos 3 ensaios calorimétricos.

Os resultados obtidos foram comparados com os valores das entalpias de solução para o 2-bromo-2-metilpropano [3] nos mesmos solventes e avaliado o efeito do tamanho da molécula de soluto no processo de solução.

Os resultados termoquímicos foram ainda analisados para os dois solutos em termos de relações lineares de energia de solvatação do tipo:

$$\Delta_s H^{\infty} = f\ (\text{descritores de solvente})$$

Com base numa análise estatística cuidada, foram feitas inferências sobre os mecanismos de interacção soluto-solvente-solvente dominantes nos processos de solução em estudo.

BATCHHEAT: SOFTWARE FOR PINCH ANALYSIS FOR BATCH PROCESS

Ana Pires[a]; Maria C. Fernandes[b]; Henrique A. Matos[b]; Clemente Pedro Nunes[b]

[a] Departamento de Engenharia Química, ISEL, Lisboa, Portugal

[b] Departamento de Engenharia Química , IST, Lisboa, Portugal

Publicado em: *Proceedings do* EPMESC IX: *The 9th International Conference on Enhancement and Promotion of Computational Methods in Engineering and Science*, 641-647, Macau, China, Novembro 2003.

Pinch Analysis extensively used in continuous process was applied in this work to a discontinuous process. The intermittent nature of batch processes imposes a three-dimensional data treatment in terms of enthalpy, temperature and time, which brings up high complexity, making manual calculation very difficult and extensive. Therefore the main purpose of this work was to develop a software package, BatchHeat, incorporating Pinch Analysis and enabling the automatic application of this methodology to a discontinuous problem. The BatchHeat, may be used as a first tool during the course of a Process Integration study. The results obtained highlight the energy inefficiencies in the process and therefore enable to set the scope for possible heat recovery, through direct heat exchange or storage.

***Keywords*: Process Integration, Pinch, Software and Batch Process**

HENRY COEFFICIENTS OF HYDROCARBONS IN WATER

Maria Celeste C. Serra,[a,b] A. M. F. Palavra[a]

[a]Centro de Química Estrutural, IST, Lisboa, Portugal

[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Proceedings JETC8, Joint European Thermodynamics Conference 8, Barcelona, Espanha, Setembro 2003.*

Henry coefficients of methane, ethylene, propene and 1-butene in water, in the temperature range from 293.15 to 323.15K were carried out in Ben-Naim/Baer type apparatus with a precision of ±0,3%. These results were compared with those predicted from the scaled particle theory (SPT). The agreement was quite good for methane and ethylene with an average deviation of about ±4%. For 1-butene in water, the agreement was also satisfactory, with an average deviation ±8%. However, the predicted Henry coefficients for propene in water were about 47% higher than the experimental ones. For this system, the prediction power of SPT can be substantially improved by introducing temperature dependent size parameters.

Keywords: Henry coefficients, Hydrocarbons, SPT.

GROWTH OF METAL PARTICLES WITHIN ZEOLITE PORES: THE EFFECT OF THE PRESENCE OF BASIC ADDITIVES

C. Bisio[a], E.R. Silva[b] , V. Dal Santo[c], G. Martra[a], S. Coluccia[a], P. Massiani[d], M. F. Ribeiro[b], J.M. Silva[e], L. Stievano[d], R. Psaro[c]

[a] Dipartimento di Chimica IFM, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy

[b] Departamento de Engenharia Química, Instituto Superior Técnico, Av. Rovisco Pais 1049-001 Lisboa, Portugal
[c] CNR-ISTM, Via C. Golgi 19, 20133 Milano, Italy
[d] Laboratoire de Réactivité de Surface, Université Paris VI, UMR 7609, 75252 Paris, France
[e] Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Proceedings do EuropaCat VI, Innsbruck, Austria, August 31 – September 04, 2003.*

Introduction: Pt-Cs/BEA zeolites are attracting catalysts for the conversion of n-hexane and n-heptane in benzene and toluene, respectively, as their performances approach those of Pt/KL zeolites, employed for these processes on the industrial scale. In a previous study we found that the catalytic activity of Pt-Cs/BEA zeolites strongly depends on the extent of basification of the zeolite pores by exchange with Cs$^+$ or impregnation with CsOH, which produces significant differences in the properties of the Pt particles encapsulated in the zeolite. Due to the apparent key role on the metal-basic phase interaction, we proceeded further in the investigation of the growth of Pt particles in contact with basic sites. Materials: H-BEA zeolite was exchanged with Cs$^+$ and Pt^{2+} (hereafter: Pt-Cs(ex)/BEA sample). From this material, different samples with increasing amount of basic component were prepared by incipient wetness impregnation with CsOH, followed by calcination (hereafter: Pt-Cs(im)/BEA samples). Results and Discussion. IR spectra of adsorbed CO$_2$ indicated that in Pt-Cs(ex)/BEA the basic sites are the framework oxygen atoms neighbor to Cs$^+$ ions, while two other types of basic sites are present in the Pt-Cs(im)/BEA, likely corresponding to surface sites of Cs$_2$O nanoparticles within the pores. By monitoring the surface state of Pt particles by IR spectroscopy of adsorbed CO, it was concluded that in all catalysts the nucleation of Pt particles begins in sites close to basic framework oxygen atoms. Due to the inter-cavities mobility possible under reduction conditions, in Pt-Cs(im)/BEA samples Pt particles/atoms migrate to the surface of Cs$_2$O nanoparticles co-encapsulated in the pores, where they are preferentially stabilized, with a significant effect on both the surface electronic state (in terms of an enrichment in electronic charge) and the size of the metal particles, which decreases from 1.8 nm to 1.2 nm as the content in the basic component increase.

MULTIPERIOD SYNTHESIS AND OPERATIONAL PLANNING OF UTILITY SYSTEMS WITH ENVIRONMENTAL CONCERNS

A. P. Oliveira Francisco[1] and H. A. Matos[2]

[1]Dep. de Eng. Química, Inst. Sup. de Engenharia de Lisboa, 1949-014 Lisboa, Portugal
[2]Dep. de Engenharia Química, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

Publicado em: *Proceedings* do *European Symposium on Computer Aided Process Engineering – 13*, *ESCAPE-13*, *Lappeenranta, Finland, 1-4 June, 2003.*

Utility plants supply the required energy demands to industrial processes. Several authors were addressed the synthesis and design of those plants. However, a multiperiod model for utility systems including environmental concerns wasn't described until now.

This paper presents an extension of Iyer and Grossmann (1997, 1998) model to synthesis and multiperiod operational planning in order to include the global emissions of atmospheric pollutants issues coming from the fuels burning.

A new four steps algorithm is introduced to solve this multiobjective model. One motivation example enables us to compare the different units and fuel selection and also the operation periods of an industrial utility system taking in account the electrical power import/export policy and environmental concerns.

KEYWORDS
Utility Systems, Process Synthesis, Multiperiod, Global Emissions, MILP.

ADAPTIVE NONLINEAR CONTROL OF A DISTRIBUTED COLLECTOR SOLAR FIELD

J. M. Igreja,[a] J. M. Lemos,[b] M. Barão ,[c] R. N. Silva,[d]
[a] Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[b] INESC-ID , Lisboa, Portugal
[c] INESC-ID, Lisboa, U. de Évora, Évora, Portugal
[d] FCT-UNL,,Monte da Caparica, Portugal

Publicado em: *Proceedings do 7th EUROPEAN CONTROL CONFERENCE 2003, University of Cambrigde, UK, September 2003.*

This paper is concerned with an application of nonlinear adaptive techniques to temperature control in a distributed collector solar field. By explicitly considering the distributed parameter character of the plant (amounting to a space dependency), certain difficulties (e.g. oscillations of the manipulated variables or excessive overshoot) arising when using a black-box approach may be overcome. In the approach followed, the partial differential equation describing the field is approximated by a lumped parameter bi-linear model, whose states are the temperature values along the field. By using feedback exact linearization with a Lyapunov approach, an adaptive controller is design. This paper improves on previous work by using a better approximated model which takes into account that, in the field considered, temperature measures are only taken at the input and at the output and not along the pipe. This allows faster convergence of parameter estimated and improved transient response. The advantages of the new algorithm proposed are illustrated by means of simulations performed in a detail physical model of the plant.

Keywords: Nonlinear Control, Adaptive Control, Solar Energy, Distributed Parameter Systems, Control Applications.

SOD ACTIVITY, "CYTOCHROME P-450", "CYTOCHROME P-450" REDUCTASE AND SECONDARY METABOLITES – CHEMICAL AND BIOLOGICAL PROPERTIES IN MUSHROOM NUTRITION

Amin Karmali
Secção de Biotecnologia, Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Proceedings of 5th International Symposium on Mushroom Nutrition, "Mushroom Nutrition: A new class of clinical nutrition", Westminster University, London, UK, June 14th, 2003 (pg. 18-24)*

Mushrooms have been known to possess medicinal properties for thousands of years. Higher basidiomycete mushrooms have been used in clinical nutrition because they exhibit anti-tumour, immune modulating, cardiovascular and anti- microbial activities (1).

The benefits of mushroom nutrition on these clinical conditions has attracted great interest in the scientific community in the last decade in order to understand the molecular mechanism responsible for their action (2).

Mushroom biomass contains many complex substances of therapeutic interest such as protein-bound polysaccharide complexes (i.e PSK, PSP and Lentinan), secondary metabolites (i.e terpenes, alkaloids and lactones) and enzymes (i.e laccase, superoxide dismutase, glucose oxidase and peroxidase) (3,4).

It has been known that enzyme therapy plays an important role in several clinical conditions such as in cancer treatment, malignant lymphoma and cardiovascular disorders (5,6).

A number of pathological damages such as carcinogenesis and cellular degeneration related to aging process are due to reactive oxygen species (ROS) produced by sunlight, ultraviolet radiation, chemical reactions and metabolic processes. These reactive oxygen species (i.e superoxide radicals) are toxic to living cells since they oxidize and degrade important biological macromolecules such as lipids and proteins. Superoxide dismutase (SOD) catalyses the destruction of superoxide radicals and hence protects oxygen - metabolizing cells from the harmful effect of these free radicals. Several research workers have shown that SOD is involved in some diseases such as Parkinson's disease, cancer and anemia. Several mushrooms have shown to-contain substances which mimick SOD activity (7,8).

Another important enzyme system consist of “cytochrome P-450” which is located in the endoplasmic reticulum and play an important role in metabolism and detoxification of endogenous substances (9). This enzyme system has been also found in some higher basidiomycete fungi.

Thrombin is an important protease of the coagulation system and therefore it is a suitable target for inhibition of blood coagulation. There are a number of secondary metabolites in mushrooms which play an important role as thrombin inhibitor. Thrombin is an important protease of the coagulation system and therefore it is a suitable target for inhibition of blood coagulation. There are a number of secondary metabolites in mushrooms which play an important role as thrombin inhibitors (10).

In the present work, we investigated the levels of SOD, “cytochrome P-450”, “cytochrome P-450” reductase (NADPH dependent) and secondary metabolites as thrombin inhibitors in MRL products *(Coriolus versicolor, Cordyceps sinensis, Ganoderma lucidium* (Reishi) and *Grifola frondosa* (Maitake) by simulating the intestinal tract of the human body.

The data presented reveal that the simulation of intestinal tract (pepsin and trypsin) decreases the enzyme and secondary metabolites's levels by a factor in the range of 15-20% .

SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF BIXIN FROM ANNATTO SEEDS

B.P. Nobre,[a] E.M.Queiroz,[b] F.L.P. Pessoa,[b] J.P. Coelho,[c] A.F.Palavra,[d] R.L.Mendes[a]

[a] Departamento de Energias Renováveis, INETI, Lisboa, Portugal
[b] DEQ/EQ/UFRJ, Rio de Janeiro, Brazil
[c] DEQ/ISEL, Lisboa, Portugal
[d] Centro Química Estrutural, IST, Lisboa, Portugal

Publicado em: *Proceedings of the 6 th International Symposium on Supercritical Fluids - Institut National Polytechnique de Lorraine, Fance ,April 2003, pp. 117-122.*

Supercritical CO_2 extraction of the pigments from annatto seeds was carried out at a pressure of 200 bar and temperature of 40 ºC using two flow rates. The efficiency of the extraction was low for the conditions studied. However, the solubility of bixin in CO_2 modified with ethanol (5 mol %) was determined, having been verified a high increase relatively to the solubility in pure CO_2.

Therefore, supercritical fluid extraction of the pigments from annatto seeds using CO_2 containing 5 mol % of ethanol was carried out at pressures of 200 and 300 bar and temperatures of 40 and 60 ºC. The extraction efficiency using the modified supercritical fluid was higher than that obtained with pure supercritical CO_2. The extraction yield increased with pressure and temperature. On the other hand, it decreased with flow rate.

To assess both the efficiency and selectivity of bixin extraction from a matrix with higher solute bulk concentration, an annatto preparation was obtained from annatto seeds, and submitted to supercritical fluid extraction using the same modified solvent. The efficiency of the extraction was similar to that obtained when annatto seeds were used, but the pigment concentration in the supercritical extracts was higher.

CALCULATION OF SOLUBILITY FOR SYSTEMS CONTAINING BIXIN, β- CAROTENE AND SUPERCRITICAL CARBON DIOXIDE

E.M.Queiroz,[a] B.P. Nobre,[b] R.L.Mendes,[b] J.P. Coelho,[c] A.F.Palavra,[d] F.L.P. Pessoa,[b]

[a]DEQ/EQ/UFRJ, Rio de Janeiro, Brazil
[b]Departamento de Energias Renováveis, INETI, Lisboa, Portugal
[c]DEQ/ISEL, Lisboa, Portugal
[d]Centro Química Estrutural, IST, Lisboa, Portugal

Publicado em: *Proceedings of the 6 th International Symposium on Supercritical Fluids - Institut National Polytechnique de Lorraine, Fance ,April 2003, pp. 741-746*

Thermodynamic modelling of solid solubility in supercritical fluids is normally limited to pure solids. Even in the presence of solid mixtures, its is considered that the different solids in the mixture behave as if they were alone, that is, they do not interact. Results in the literature show that hypothesis is true if the molecules if the solutes have some symmetry, both in size or polarity. The aim of this work is to present a thermodynamic model for a very asymmetric system consisting of two solids (β-carotene and bixin) and supercritical solvent (carbon dioxide). This system is very complex and the nonideallity happens due to the difference of the sizes of the molecules and their polarities. The model is based on Peng-Robinson equation of state and depends on the critical properties and the binary interaction parameters. These parameters between carbon dioxide and β-carotene and between carbon dioxide bixin were obtain from binary experimental data presented in the literature. For the solid mixture, β-carotene and bixin, the model without any solid interaction describes

poorly the available experimental data (approximately 75% of average desviation). Then, a model considering an interaction between the components in the solid phase and relaxing the constraint of equal interaction parameters between the solutes was tested and able to better describe the experimental data behaviour, with a deviation of 20% for the bixin and 45% for the β-carotene.

ISOCHORIC (P, ρ, T) MEASUREMENTS OF FLUIDS AND THEIR BINARY MIXTURES AT HIGH PRESSURES AND TEMPERATURES

M.B.F. Mourato,[a] J.A.P. Coelho,[b] M.A.T. Cardoso,[a] A.M.F.Palavra,[a]

[a]DEQ/IST, Lisboa, Portugal
[b]DEQ/ISEL, Lisboa, Portugal

Publicado em: *Proceedings of the 8 th Joint European Thermodynamics Conference – Universitat Autònoma de Barcelona, Barcelona, Espanha , September 2003, pp. 197-201*

The knowledge of the equation of state of pure fluids and their mixtures is of great importance in Science and Engineering. Many experimental studies have been carried out in this area at low and room temperature. However, the situation is rather different at high temperatures. A comprehensive programs of (p,ρ, T) measurements on binary mixtures of molecular fluids (Ar, N_2, CH_4, C_2H_6, CO, etc…) at high temperatures was implemented, recently, in the Laboratory of Experimental Thermodynamics (Lisbon, Portugal), using the isochoric method. These (p,ρ,T) measurements, together with those carried out at low temperatures, involving the same binary mixtures, will provide a better knowledge of the intermolecular potential for these simple molecules. Moreover, some of these isochoric studies will be relevant to the design of equipment, mainly in coal conversion. The aim of this work is to present accurate isochoric (p,ρ, T) measurements carried out in our laboratory at high pressure and temperatures.

SUPERCRITICAL CO_2 SUPERCRITICAL OF γ-LINOLENIC ACID FROM THE CYANOBACTERIUM *ARTHROSPIRA MAXIMA*. EXPERIMENTS AND MODELING.

R.L.Mendes,[a] A.D. Reis,[a] M.T. Cardoso,[b] A.P.Pereira,[b] A.F.Palavra,[b] J.P. Coelho,[c]

[a]Departamento de Energias Renováveis, INETI, Lisboa, Portugal
[b]DEQ/IST, Lisboa, Portugal
[c]DEQ/ISEL, Lisboa, Portugal

Publicado em: *Proceedings of the 8 th Joint European Thermodynamics Conference – Universitat Autònoma de Barcelona, Barcelona, Espanha , September 2003, pp. 183-188*

The freeze-dried biomass of *Arthrospira* was submitted to supercritical CO_2 extraction, in a flow apparatus, at temperatures of 50 and 60 ºC, pressures of 250 and 300 bar and flow-rates of 12.8, 19.6 and 29.5 g CO_2/min. The achieved extraction yield in lipids, using pure CO_2, was low and increased slightly with pressure and temperature and decreased with the flow rate.

In order to increase the extraction yield of lipids, namely GLA, which is mostly contained in glycolipid fractions, a polar compound (ethanol) was mixed with the freeze-dried biomass. The presence of ethanol increased both lipid and GLA yields relatively to the extraction with pure CO_2. A plug flow model, in which only the resistance to internal mass transfer is considered, was applied to the supercritical CO_2 extraction of the lipids from this biomass.

SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF *FOENICULUM VULGARE* VOLATILE OIL

J.A.P. Coelho,[a,b] A.P. Pereira,[a] R.L. Mendes,[c] A.M.F. Palavra[a]

[a]Centro Química Estrutural, IST, Lisboa, Portugal
[b]Departamento de Engenharia Química/ISEL, Lisboa, Portugal
[c]Departamento de Energias Renováveis, INETI, Lisboa, Portugal

Publicado em: *Flavour an Fragrance Journal*, **2003**, 18, 316-319.

Supercritical fluid extraction (SFE) with CO_2 of volatile oil from fennel (*Foeniculum vulgare* ssp. *piperitum* (Ucria) Coutinho) was carried out at temperatures of 40 and 50 ºC and pressures of 90 and 100 bar in a flow apparatus using a two-stage fractional separation technique. The best conditions of extraction (pressure P=90 bar and

temperature, T=40 ºC) and of separation (P=80 bar, T=-10ºC for the first separator and P=20 bar, T=-10ºC for the second) were used to assess the effect of different mean particle size and flow rate of CO_2. The yield of the extraction and composition of the volatile oil were compared with those obtained by hydrodistillation. The study showed that the particle size of the fruits does not practically affect either the yield or the composition of the oil, with the exception of the presence of a small amount of waxes in the volatile oil extracted by SFE from the fruits presenting the highest particle size. Further, increasing of the flow rate of CO_2 does not seem to influence the composition, although it increases the rate of extraction, thus leading to a decrease of the extraction time. The fennel oil was analysed by gas chromatography (GC) and chromatography-mass spectrometry (GC-MS). The main compounds identified in the oils were fenchone (17%), estragol (21%) and (E)-anethole (43%).

Keywords: *Foeniculum vulgare*, fennel, essential oil, supercritical extraction, fractionation.

LYCOPENE AND β-CAROTENE EXTRACTION FROM TOMATO PROCESSING WASTE USING SUPERCRITICAL CO_2

E. Sábio,[a] M. Lozano,[b] V. Montero de Espinosa,[b] R.L. Mendes,[c] A.P.Pereira,[d] A.M.F. Palavra,[d] J.A.P. Coelho,[d,e]

[a]Escuela Ingenierias IndustrialesI/Universidade da Extremadura, Espanha
[b]Instituto Tecnológico Alimentar, Badajoz, Espanha
[c]Departamento de Energias Renováveis, INETI, Lisboa, Portugal
[d]Centro de Química Estrutural/IST, Lisboa, Espanha
[e]Departamento de Engenharia Química/ISEL, Lisboa, Portugal

Publicado em: *Ind. Eng. Chem. Res.* **2003**, 42, 6641-6646.

Tomato skins and their mixtures with seeds were submitted to supercritical CO_2 extraction using a flow apparatus at the pressures of 250 and 300 bar and temperatures of 60 and 80 ºC. Two different mean particle sizes (80 and 345 μm) were used at two solvent flow rates (0.792 and 1.35 kg/h). The yields of lipids, lycopene and β-carotene obtained by supercritical fluid extraction were compared with those obtained with the conventional organic solvent extraction. Supercritical fluid extraction from tomato skins, at 300 bar and 80 ºC, allowed the recovery of 80 % of lycopene and 88 % of β-carotene, using about 130 g of CO_2 per gram of matrix, at the lower flow rate of CO_2.

Keyword: ***supercritical carbon dioxide, tomato waste, extraction, lycopene, β-carotene***

NANOCOMPOSITE CATALYTIC MATERIALS: SYNTHESIS, CHARACTERISATION AND REACTIVITY OF PT/CS-BEA ZEOLITES

C. Bisio [a], C. Caldeira [b], V. Dal Santo [c], G. Martra [a], P. Massiani [d], R. Psaro [c], M.F. Ribeiro [b], J.M. Silva [e], L. Stievano [d]
[a]Dipartimento di Chimica IFM, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy
[b]Departamento de Engenharia Química, Instituto Superior Técnico, Av. Rovisco Pais 1049-001 Lisbon, Portugal
[c]CNR-ISTM, Via C. Golgi 19, 20133 Milan, Italy
[d]Laboratoire de Réactivité de Surface, Université Paris VI, UMR 7609, 75252 Paris, France
[e]Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, R. Cons. Emídio Navarro, 1950-062 Lisbon, Portugal

Publicado em:*Inorganica Chimica Acta***, 2003***, 349, 227-238.*

A parent acidic H-BEA sample characterised by crystallites with very small sizes and high external surface area has been used to prepare a series of Pt/Cs-BEA catalysts. The exchange three times of the highly defective H-BEA in a 0.5 M CsCl solution allowed to exchange only about half of the protons, as evaluated from both chemical analysis and FTIR spectroscopy in the presence of adsorbed NH_3. The further exchange by $Pt(NH_3)_4^{2+}$ followed by impregnation with CsOH, calcination and finally reduction, led to a series of Pt/Cs-BEA samples with progressive increase of the caesium loading and concomitant change of the reducibility of the calcined Pt species and decrease of the size of the reduced Pt particles. The analysis of the FTIR data in the nOH and dNH ranges indicates a progressive removal of the protons. Finally, the selectivities to cracking, isomerisation, and aromatisation during conversion of n-hexane are in line with the variations of acido/basicity and Pt particle sizes in the samples.

CHARACTERIZATION OF THE ACIDITY OF AL- AND ZR-PILLARED CLAYS

Ana P. Carvalho [a], Ângela Martins [b], João M. Silva [b], João Pires [a], Helena Vasques [b], M. Brotas de Carvalho [a]
[a]Departamento de Química e Bioquímica da Faculdade de Ciências da Universidade de Lisboa, Ed. C8, piso 6, Campo Grande, 1749-016 Lisboa, Portugal
[b]Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, R. Cons. Emídio Navarro, 1950-062 Lisbon, Portugal

Publicado em: *Clays and Clay Minerals***, 2003***, 51, 340-349.*

The surface acidic properties of pillared clays (PILCs) with Al or Zr oxide pillars (prepared from a natural Portuguese smectite and a synthetic Laponite), and of a protonic NaHY zeolite, were studied by two methods: pyridine adsorption followed by infrared (IR) spectroscopy, and the catalytic transformation of 1-butene. The results of the pyridine adsorption revealed that all the pillared clays studied have mainly Lewis-type acidity, the exception being the clay pillared with Zr oxide, obtained from natural smectite, which also presents a significant number of Bronsted acid sites. The results of 1-butene transformation showed that the pillared clays exhibit catalytic properties similar to those of the protonic Y zeolite. The acid character of the solids was confirmed by the values of the cis/trans 2-butene isomers ratio. At short reaction times, product distribution showed that the main reaction is oligomerization, followed by cracking. After 15 min the products are mainly the linear isomers, cis and trans-2-butene, showing that the majority of the catalytic active sites, are already poisoned after 15 min of reaction. The particular behaviour of Laponite intercalated with Al oxide pillars is discussed. The IR spectra of the pyridine adsorbed on the fresh samples and after the catalytic assays, revealed that Lewis acid sites behave as active sites for 1-butene catalytic transformation. The consistency between the results of the two complementary techniques used for the characterization of the acidity of the solids was proved.

NOVEL LASER-INDUCED LUMINESCENCE RESULTING FROM BENZOPHENONE /*O*-PROPYLATED *p-tert*-BUTYLCALIX[4]ARENES COMPLEXES. A DIFFUSE REFLECTANCE STUDY.

L.F. Vieira Ferreira[a,*], M.R. Vieira Ferreira[b], J.P. Da Silva[a,c], I. Ferreira Machado[a], A.S. Oliveira[a], J.V. Prata[b]

[a]Centro de Química-Física Molecular - Complexo Interdisciplinar, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

[b]Secção de Química Orgânica, Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, R. Conselheiro Emídio Navarro, 1950-062 Lisboa, Portugal

[c]FCT, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

Publicado em: *Photochem. Photobiol. Sci.,* **2003**, *2, 1002-1010.*

Laser-induced room temperature luminescence of air-equilibrated benzophenone/*O*-propylated *p-tert*-butylcalix[4]arene solid powdered samples revealed the existence of a novel emission, in contrast with benzophenone/*p-tert*-butylcalix[4]arene complexes, where only benzophenone emits. This novel emission was identified as phosphorescence of 1-phenyl-1,2-propanedione, which is formed as the result of an hydrogen atom abstraction reaction of the triplet excited benzophenone from the propoxy substituents of the calixarene.

Room temperature phosphorescence was obtained in air-equilibrated samples in all propylated hosts. The decay times of the benzophenone emission vary greatly with the degree of propylation, the shortest lifetimes being obtained in the tri and tetrapropylated calixarenes.

Triplet-triplet absorption of benzophenone was detected in all cases, and is the predominant absorption in the *p-tert*-butylcalix[4]arene case, where an *endo*-calix complex is formed. Benzophenone ketyl radical formation occurs with the *O*-propylated *p-tert*-butylcalix[4]arenes hosts, suggesting a different type of host/guest molecular arrangement.

Diffuse reflectance laser flash photolysis and gas chromatography-mass spectrometry techniques provided complementary information, the former about transient species and the latter regarding the final products formed after light absorption. Product analysis and identification clearly show that the two main degradation photoproducts following laser excitation in the propylated substrates are 1-phenyl-1,2-propanedione and 2-hydroxybenzophenone, although several other minor photodegradation products were identified. A detailed mechanistic analysis is proposed.

While the solution photochemistry of benzophenone is dominated by the hydrogen abstraction reaction from suitable hydrogen donors, in these solid powdered samples, the α-cleavage reaction also plays an important role. This finding occurs even with one single laser pulse which lasts only a few nanoseconds, and is apparently related with the fact that scattered radiation exists, due to multiple internal reflections possibly trapping light within non-absorbing microcrystals in the sample, and is detected until at least 20 μs after the laser pulse. This could explain how photoproducts thus formed could also be excited with only one laser pulse.

HIGH FIRST POLARISABILITY AND PERFECTLY ALIGNED CRYSTAL PACKING FOR AN ORGANOMETALLIC COMPOUND $[Fe(\eta^5\text{-}C_5H_5)((R)\text{-PROPHOS})(p\text{-}N{\equiv}CC_6H_4NO_2)][PF_6].CH_2Cl_2$

W. Wenseleers[a], E. Goovaerts[a,*] P. Hepp[a], M.H. Garcia[b,c], M.P. Robalo[b,d,1], A.R. Dias[b], M.F. Piedade[b,c], M.T. Duarte[b]
[a]Physics Department, University of Antwerp (UIA), Wilrijk-Antwerpen, Belgium
[b]Centro de Química Estrutural, IST, Lisboa, Portugal
[c]Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal
[d]Departamento de Química, Universidade de Évora, Évora, Portugal
[1] Present adress: Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Chem. Phys. Letters*, **2003**, 367, 390-397.

The molecular first hyperpolarizability, *β*, and the X-ray crystal structure of the complex $[Fe(\eta^5\text{-}C_5H_5)((R)\text{-PROPHOS})(p\text{-}NCC_6H_4NO_2)][PF_6]$ ((R)-PROPHOS = (R)-(+)-bis-(1,2-diphenylphosphino)propane) were determined. A near-resonant enhanced *β* value as high as 545×10^{-30} esu was obtained from hyper-Rayleigh scattering measurements. In addition, the compound crystallises in the space group P1 with a perfect alignment of the dipolar molecules (only a single chromophore per unit cell), thus maximizing the macroscopic nonlinearity for electro-optic or parametric frequency conversion applications. The molecular packing in the crystal is analyzed in order to understand the factors leading to the perfect alignment.

SYNTHESIS, CHARACTERISATION OF (ARENE)TRICARBONYLCHROMIUM COMPLEXES LINKED TO CATIONIC FE AND RU DERIVATIVES AND STUDIES OF FIRST HYPERPOLARISABILITIES BY HYPER-RAYLEIGH SCATTERING

M.H. Garcia[a,b*], S. Royer[b], M.P. Robalo[b,c*], A.R. Dias[b], J.-P. Tranchier[d], R. Chavignon[d], D. Prim[d], A. Auffrant[d], F. Rose-Munch[d], E. Rose[d*], J. Vaissermann[e], A. Persoons[f], I. Asselberghs[f]
[a]Departamento de Química e Bioquímica, FCUL, Lisboa, Portugal
[b]Centro de Química Estrutural, IST, Lisboa, Portugal
[c]Departamento de Engenharia Química, ISEL, Lisboa, Portugal
[d]Lab. de Synthèse Organique et Organometallique, UMR CNRS, Paris, France
[e]Lab. de Chimie Inorganique et Matériaux Moléculaires, UMR CNRS, Paris, France
[f] Center for Research on Molecular Electronics and Photonics, University of Leuven, Leuven, Belgium

Publicado em: *Eur. J. Inorg. Chem.*, **2003**, 3895-3904.

In order to investigate the non-linear optical properties, in particular second-order effects of binuclear organometallic complexes, a series of new cationic binuclear $[MCp(DPPE)N{\equiv}C\text{-(spacer)-}C{\equiv}C\text{-}C_6H_5Cr(CO)_3]^+[PF6]^-$ compounds and mononuclear precursors $[N{\equiv}C\text{-(spacer)-}C{\equiv}C\text{-}C_6H_5Cr(CO)_3]$ have been synthesised [where M = FeII or RuII; Cp = $\eta^5\text{-}C_5H_5$ and spacer = phenyl ring (C_6H_4), thiophene, (C_4H_2S), or bithiophene ($(C_4H_2S)_2$)]. The Fe or Ru organometallic σ-donor fragments were linked by an extended π system to the acceptor $Cr(CO)_3$ fragment. The effect of π back-donation involving the second Fe or Ru metal centre and the π* orbitals of the N≡C-coordinated group, was probed by the ν(N≡C) stretching bands on the IR spectra and also by NMR spectroscopic data. The planarity, largely due to the π-electron resonance, found on the solid state structure of the mononuclear complex $[N{\equiv}C\text{-}C_6H_5\text{-}C{\equiv}C\text{-}(\eta^6\text{-}C_6H_5)Cr(CO)_3]$ (**1Cr**) determined by X-ray diffraction [monoclinic system, $P21/c$ space group, with a = 10.326(2) A° , b = 13.209(5) A°, c = 11.799(2) Aº and Z = 4] emphasises the electronic effect of this building block. The significant values of first hyperpolarisability β determined by hyper-Rayleigh scattering (HRS) indicate that the Fe containing compounds were more efficient on second-order non-linear optical properties than the ruthenium analogues and the parent mononuclear chromium compounds.

CYANIDE AS A VERSATILE LEWIS BASE LIGAND AT A DINITROGEN – BINDING IRON (II) CENTRE: MONO – AND HETERONUCLEAR ADDUCTS

Sílvia[a,b] S. P. R. Almeida, M. Fátima Guedes da Silva[b], Lucjan Jerzykiewicz[c], Piotr Sobota[c] and Armando J.L. Pombeiro[b]
[a]Instituto Superior de Engenharia de Lisboa, Lisboa, Portugal.
[b]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Lisboa, Portugal.
[c]Faculty of Chemistry, University of Wroclaw, Wroclaw, Poland.

Publicado em: *Inorganica Chimica Acta*, **2003**, 356, 259-266.

The ligand cyanide in *trans* – $[FeH(CN)(dppe)_2]$ is activated towards aroylation, alkylation and addition of various transition metal Lewis acids, in particular $[WCl_4(PPh_3)_2]$, $[ReOCl_3(PPh_3)_2]$, $[PdCl_2(PPh_3)_2]$ and $[PtCl(Ph)(PPh_3)_2]$, to give, in the former case, mononuclear isocyanide complexes and, in the latter case, heteronuclear adducts with bridging cyanide. Their syntheses and spectroscopic characterization are presented, as well as of the X-ray diffraction analyses of a trinuclear complex witn the $\{Fe{-}C{\equiv}N{-}W{-}N{\equiv}C{-}Fe\}$ unit and the parent cyano *trans* – $[FeH(CN)(dppe)_2]$ complex. The cyanide bridge allows the electronic communication between the metal centres as indicated by a cyclic voltammetry study.

ELECTROCHEMICAL BEHAVIOUR OF *trans* – [FeH(CN)(dppe)$_2$] ADDUCTS

Sílvia S. P. R. Almeida[a,b], M. Fátima C. Guedes da Silva[b] and Armando J. L. Pombeiro[b]
[a]Instituto Superior de Engenharia de Lisboa, Lisboa, Portugal.
[b]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Lisboa, Portugal.

Publicado em: *Collect. Czech. Chem. Commun.*, **2003**, 68, 1663-1676.

Electrochemical behaviour of various metallo cyano adducts of *trans* – $[FeH(CN)(dppe)_2]$ *viz.* the dinuclear complexes *trans* – $[FeH(dppe)_2(\mu\text{-}CN)PdCl_2(PPh_3)]$, $[FeH(dppe)_2(\mu\text{-}CN)NiCl_2(PCy_3)]$, and trinuclear $[\{FeH(dppe)_2(\mu\text{-}CN)\}_2(ReOCl_3)]$, $[\{FeH(dppe)_2(\mu\text{-}CN)\}_2(PtCl(Ph)]$, and $[\{FeX(dppe)_2(\mu\text{-}CN)\}_2\text{-}WCl_3(OH)]$, (X = Cl or OH, dppe = 1,2 – diphenylphosphinoethane, and $PCy_3 = P(C_6H_{11})_3$, as well as the benzoylisocyanide mononuclear adduct of *trans* – $[FeH(CNCOPh)(dppe)_2]$, is reported. All of them exhibit Fe^{II}/Fe^{III} – based oxidations (which are reversible, except for *trans* – $[FeH(CNCOPh)(dppe)_2]$. The metallocyanide bridges $C{\equiv}N - Re - N{\equiv}C$ and $C{\equiv}N{-}W{-}N{\equiv}C$ in $[\{FeH(dppe)_2(\mu\text{-}CN)\}_2(ReOCl_3)]$ and $[\{FeX(dppe)_2(\mu\text{-}CN)\}_2\ WCl_3(OH)]$, respectively, allow electronic communication between the iron centres, with possible generation of mixed – valence Fe^{II}/Fe^{III} complexes whose comproportionation constant could be estimated in the former case. From the values of the measured oxidation potentials, the electrochemical P_L and E_L ligand parameters have been estimated for the metallocyanide ligands that were shown to behave as stronger net electron donors than organoisocyanides, although

weaker than cyanide itself. Ligand – centred reduction processes were also observed to lead, in the cases of complexes *trans* – [FeH(CNCOPh)(dppe)$_2$] (CNCOPh – based reduction) and [FeH(dppe)$_2$(μ-CN)PdCl$_2$(PPh$_3$)] (Pd^{II} – based reduction in the CNPdCl$_2$(PPh$_3$)$^-$ metallocyanide ligand), to the dissociation of the adduct, with regeneration of the parent cyano complex *trans* - [FeH(CN)(dppe)$_2$], thus reflecting the reductive decrease of the electrophillic (or Lewis acidic) character of the benzoyl and {CNPdCl$_2$(PPh$_3$)} groups.

SYNTHESES AND PROPERTIES OF HYDRIDE-CYANAMIDE AND DERIVED HYDROGEN-CYANAMIDE COMPLEXES OF MOLYBDENUM(IV). CRYSTAL STRUCTURE OF [MoH$_2$(NCNH$_2$)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][BF$_4$]$_2$

L. M. D. R. S. Martins[a,b], E. C. B. A. Alegria[a,b], D. L. Hughes[c], J. J. R. Fraústo da Silva[a] and A. J. L. Pombeiro[a]

[a] Centro de Química Estrutural, IST, Lisboa, Portugal
[b] Secção de Química Inorgânica, DEQ, ISEL, Lisboa, Portugal
[c] Biological Chemistry Department, John Innes Centre, Norwich, U. K.

Publicado em: *Dalton Trans.,* **2003**, 3743-3750.

The first hydride-cyanamide (or -cyanoguanidine) complexes of molybdenum, [MoH$_2$(NCR)$_2$(dppe)$_2$][BF$_4$]$_2$ (R = NH$_2$ **1a**, NMe$_2$ **1b**, NEt$_2$ **1c** or NC(NH$_2$)$_2$ **1d**; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$), have been prepared by treatment of [MoH$_4$(dppe)$_2$] in THF with the appropriate cyanamide (or cyanoguanidine) in the presence of HBF$_4$. Reaction of **1a** with a base leads to the bis(hydrogen-cyanamide) complex *trans*-[Mo(NCNH)$_2$(dppe)$_2$][BF$_4$]$_2$ **2** or to the bis(cyanoimide) complex *trans*-[Mo(NCN)$_2$(dppe)$_2$] **3**, *via* base-catalysed dehydrogenation (and also deprotonation for the latter product), whereas cathodically-induced dehydrogenation appears to form [MoH$_2$(NCNH)(NCNH$_2$)(dppe)$_2$]$^+$ **4**. The spectroscopic properties of the complexes are also reported along with their electrochemical behaviours and the molecular structure of **1a** as established by X-ray crystallography which indicates the presence of the NCNH$_2$ ligands involved in two hydrogen bonds connecting the ions in dimeric units.

ALLENYLIDENE AND DERIVED ALKYNYL COMPLEXES OF IRON(II) WITH THE {FeBr(Et$_2$PCH$_2$CH$_2$PEt$_2$)$_2$}$^+$ CENTRE

A. I. F. Venâncio[a], L . M. D. R. S. Martins[a,b], A. J. L. Pombeiro[a*]

[a]Centro de Química Estrutural, IST, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: J.Organomet. Chem., *2003, 684, 315-321.*

The allenylidene complexes *trans*-[FeBr{=C=C=C(R)Ph}(depe)$_2$][BPh$_4$] (depe = Et$_2$PCH$_2$CH$_2$PEt$_2$; R = Me **1**, Ph **2**) were obtained by treatment of a methanolic

solution of *trans*-[$\mathrm{FeBr_2(depe)_2}$] with the appropriate alkynol HC≡C–C(R)Ph(OH), in the presence of Na[$\mathrm{BPh_4}$]. The methylallenylidene ligand in **1** undergoes reversible deprotonation (by NaOMe) to yield the enynyl (or ene-yne) complex of iron(II), *trans*-[FeBr{–C≡C–C(=$\mathrm{CH_2}$)Ph}$\mathrm{(depe)_2}$] **3.** The diphenylallenylidene ligand in **2** undergoes regioselective hydride γ-addition on reaction with K[B{CH(Me)Et}$_3$H] to afford the alkynyl complex *trans*-[FeBr{–C≡C–C(H)$\mathrm{Ph_2}$}$\mathrm{(depe)_2}$] **4**.

REACTIONS OF CYCLIC AND LINEAR ALKYNOLS WITH A PHOSPHINIC IRON(II) CENTRE

A.I.F. Venâncio[a], L.M.D.R.S. Martins[a,b], J.J.R. Fraústo da Silva[a], A.J.L. Pombeiro[a*]

[a]Centro de Química Estrutural, Complexo I, IST, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Inorg. Chem. Commun.*, **2003**, 6, 94-96.

Treatment of a MeOH solution of *trans*-[$\mathrm{FeBr_2(depe)_2}$] (depe = $\mathrm{Et_2PCH_2CH_2PEt_2}$) with $\mathrm{HC{\equiv}CC_6H_{10}OH}$ or HC≡C$\mathrm{(CH_2)}_n$OH (n = 1 or 2), in the presence of $\mathrm{NaBPh_4}$, forms the cyclic allenylidene *trans*-[FeBr(=C=C=$\mathrm{C_6H_{10}}$)$\mathrm{(depe)_2}$][$\mathrm{BPh_4}$] or the alkyne *trans*-[FeBr{η^2-HC≡C$\mathrm{(CH_2)_n}$OH}$\mathrm{(depe)_2}$][$\mathrm{BPh_4}$] (n = 1 or 2) complexes, respectively.

ELECTROCHEMICAL STUDY OF ALKYNYL Fe(II) COMPLEXES

A. I. F. Venâncio[a], L. M. D. R. S. Martins[a,b], A. J. L. Pombeiro[a*]

[a]Centro de Química Estrutural, Complexo I, IST, Lisboa, Portugal
[b]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

Publicado em: *Port. Electroch. Acta,* **2003**, 21, 85-90.

The behaviour of the neutral alkynyl complexes *trans*-[FeBr(L)$\mathrm{(depe)_2}$] (L = –C≡C–C(=$\mathrm{CH_2}$)Ph **1*a***, –C≡C–$\mathrm{CPh_2}$(H) **1*b***; depe = $\mathrm{Et_2PCH_2CH_2PEt_2}$) is studied by cyclic voltammetry and the electrochemical P_L and E_L ligand parameters for the alkynyl ligands are estimated showing that they behave as very strong *net* electron-donors.

STATISTICAL THERMODYNAMIC APPROACH TO AUSTENITIC $Fe_{1-y}Nb_yN_x$ SYSTEM

N. Shohoji[a] and M. C. Monteiro Dias[b]

[a]Departamento de Materiais e Tecnologias de Produção, INETI, Lisboa, Portugal
[b]Laboratório de Química Inorgânica, ISEL, Lisboa, Portugal

Publicado em: ***Materials Science and Technology*, 2003**, 19, 429-434.

Available equilibrium *P–T-C* (pressure-temperature-composition) relationships reported for fcc (face centred cubic) $Fe_{1-y}Nb_yN_x$ alloys with Nb content y up to 0.00561 were analysed on the basis of statistical thermodynamics. The reported *P-T-C* relationships showed a trend of rising N level x with increasing Nb content y under comparable conditions of temperature T and nitrogen partial pressure $p(N_2)$. Statistical models assuming several types of atom clustering modes were compared. A model in which interstitial N atoms were preferentially consumed first to form Nb – N dipoles in the $Fe_{1-y}Nb_y$ lattice, and then the remaining N atoms were distributed over O sites (octahedral interstitial sites) surrounded by six Fe atoms without Nb, was concluded to be the most realistic one.

MEASURING ENZYMATIC ACTIVITY OF A RECOMBINANT AMIDASE USING FOURIER TRANSFORM INFRARED SPECTROSCOPY.

Pacheco R, Serralheiro ML, Karmali A, Haris PI.
Departamento de Engenharia Quimica, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emidio Navarro, 1, 1949-014 Lisboa, Portugal.

Publicado em: *Anal. Biochem.* **2003***, 322, 208-14.*

A method based on Fourier transform infrared spectroscopy (FT-IR) has been developed for assaying the *Pseudomonas aeruginosa* native amidase (E.C. 3.5.1.4), overproduced in an Escherichia coli strain. The kinetic of acetamide hydrolysis by the enzyme, in aqueous media, was monitored by measuring the intensity of the acetamide amide I band maximum at 1635 cm(-1) as a function of time. A value of 0.5mM(-1) cm(-1) was obtained for the extinction coefficient (epsilon) of acetamide at this frequency. The rate of the hydrolysis was found to be linear with the concentration of the enzyme up to 90 microM. The Michaelis-Menten kinetic parameters V and K(m) were determined as 30.7 U/mg and 4mM, respectively. These results were similar to those obtained using high-performance liquid chromatography analysis of the same hydrolytic reaction catalyzed by amidase either in water or in buffer. This suggests that the precision of the FT-IR method is suitable for the kinetic studies of amidase with the additional advantage of being able to perform a real-time measurement of the enzymatic activity.

SOLUBILITY OF 1-BUTENE IN WATER AND IN A MEDIUM FOR THE CULTIVATION OF A BACTERIAL STRAIN

Maria Celeste C. Serra [a, b], A.M.F. Palavra [b]

[a]Departamento de Engenharia Química, ISEL, Lisboa, Portugal

[b]Centro de Química Estrutural, IST, Lisboa, Portugal

Publicado em: *Journal of Solution Chemistry*, **2003**, 32, 527-534.

Solubility measurements of 1-butene in water, in the temperature range from 293.15 to 323.15K and at atmospheric pressure, were carried out using a Ben-Naim/Baer type apparatus. The experimental results have a precision of about ±0.3%. Using accurate thermodynamic relations, the Ostwald coefficients at the experimental conditions and at infinite dilution, the mole fractions of the dissolved gas at the gas partial pressure of 101.325 kPa and the Henry coefficients at the water vapour pressure were calculated. On the other hand, the values of the mole fraction of dissolved gas were fitted to the Clarke, Glew and Weiss equation and thermodynamic quantities, standard molar Gibbs energy, entropy and enthalpy changes, for the process of transferring the 1-butene molecules from the gaseous to the water phase were computed. Moreover, solubility measurements of 1-butene in an aqueous medium for the cultivation of *Xanthobacter* Py2 in the same temperature range were also performed at atmospheric pressure. These solubility data are approximately 2.6% lower than those observed in pure water.

Keywords: Solubility, 1-butene, Water; Thermodynamic properties; Cultivation medium; *Xanthobacter* Py2.

SIMULTANEOUS MEASUREMENT OF THE DENSITY AND VISCOSITY OF COMPRESSED LIQUID TOLUENE

Helena M.T. Avelino[1,2], João M.N.A. Fareleira[1,3], and William A. Wakeham[4]

[1] Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico,
Av. Rovisco Pais, 1049-001 Lisbon, Portugal.

[2] Permanent address: Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Rua Emídio Navarro, 1900 Lisbon, Portugal.

[3] To whom correspondence should be addressed.

[4] Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, United Kingdom

Publicado em: *Int.J.Thermophys*, **2003**, 24, 323-336.

A vibrating-wire densimeter described previously has been used to perform simultaneous measurements of the density and viscosity of toluene at temperatures from 222 to 348 K and pressures up to 80 MPa. The density measurements are essentially based on the hydrostatic weighing principle, using a vibrating-wire device operated in forced mode of oscillation, as a sensor of the apparent weight of a cylindrical sinker immersed in the test fluid. The resonance characteristics for the transverse oscillations of the wire, which is also immersed in the fluid, are described by a rigorous theoretical model, which includes both the buoyancy and the hydrodynamic effects, owing to the presence of the fluid, on the wire motion. It is thus possible, from the working equations, to determine simultaneously, both the density and the viscosity of the fluid from the analysis of the resonance curve of the wire oscillation, the density being related essentially to the position of the maximum and the viscosity to its width.

New results of measurements of the density and viscosity of toluene in the compressed liquid region are presented, and compared with literature data. The density results extend over a temperature range 222 K $<T<$ 348 K, and pressures up to 80 MPa. The viscosity results cover a temperature range of 248 K $< T <$ 348 K and pressures up to 80 MPa. The uncertainty of the present density data is estimated to be within ±0.1% at temperatures 298 K $< T <$ 350 K, and ±0.15% at 222 K $< T <$ 273 K. The corresponding overall uncertainty of the viscosity measurements is estimated to be ±2% for temperatures 298 K $< T <$ 350 K, and ±3% for 248 K $< T <$ 273 K

THE POSSIBLE ROLE OF MUSHROOM NUTRITION AS A DELIVERY AGENT FOR ENZYME THERAPY IN CANCER CARE - CHEMICAL AND BIOLOGICAL PROPERTIES OF MUSHROOM NUTRITION

Amin Karmali

Secção de Biotecnologia do Departamento de Engenharia Química do Instituto Superior de Engenharia de
Lisboa. Rua Conselheiro Emídio Navarro, Lisboa, Portugal

Publicado em: ***Mycology News*, 2003, *1(7) 7-8*.**

The use of mushroom nutrition as part of the nutritional management of cancer patients is standard practice in Japan and other Asian cultures. Recently, there have been a number of studies looking at the nutritional benefits of fungi in enhancing immune function.

Several researchers have demonstrated that protein-bound polysaccharide complexes such as PSK or PSP, derived from *Coriolus versicolor* or Lentinan derived from *Letinula edodes* are the most important component responsible for immune enhancing and anti-tumour activities of these fungi. However, other components of fungi also play an important part in their immuno-modulatory activity. For instance a 10KD peptide from *Coriolus versicolor* has been shown to mimick the activity of superoxide dismutase, thus helping to reduce oxidative stress.

It has been known for some time that enzyme therapy has important benefits for several clinical conditions, including cancer and cardiovascular disorders. From the data presented in this work, it is apparent that mushrooms are particularly rich sources of enzymes which may participate in these conditions through reduction in oxidative stress and inhibition of cell proliferation.

Teses

QUÍMICA DE COORDENAÇÃO DE ALCINÓIS E DINITRILOS EM CENTROS DE FERRO(II)
Ana Isabel Venâncio

Doutoramento em: *Química*
Grau Concedido por: *IST – Universidade Técnica de Lisboa*
Orientadores: *Armando José Lattourrette Pombeiro e Luísa Margarida Sousa Martins*
Provas Concluídas em: *15 de Dezembro de 2003*

Neste trabalho foi investigada a química de coordenação de alcinóis, alenilidenos, alcinilos, e de dinitrilos e diisonitrilos, em centros fosfínicos de Fe(II). No capítulo 1 é descrita a síntese e caracterização de compostos de alenilideno linear, *trans*-$[\mathrm{FeBr}(=\mathrm{C}=\mathrm{C}=\mathrm{CR_1R_2})(\mathrm{depe})_2][\mathrm{Y}]$ ($\mathrm{R_1}=\mathrm{Ph}$, $\mathrm{R_2}=\mathrm{Me}$; $\mathrm{R_1}$, $\mathrm{R_2}=\mathrm{Ph}$ ou Et; $\mathrm{depe}=\mathrm{Et_2PCH_2CH_2PEt_2}$, $\mathrm{Y}=\mathrm{BF_4}$ ou $\mathrm{BPh_4}$), e cíclico, *trans*-$[\mathrm{FeBr}\{=\mathrm{C}=\mathrm{C}=\mathrm{C(CH_2)}_n\mathrm{CH_2}\}(\mathrm{depe})_2][\mathrm{BPh_4}]$ (n = 4 ou 6), assim como de compostos acetilénicos do tipo *trans*-$[\mathrm{FeBr}\{\eta^2\text{-}\mathrm{HC}\equiv\mathrm{C(CH_2)}_n\mathrm{OH}\}(\mathrm{depe})_2][\mathrm{BPh_4}]$ (n = 1, 2 ou 4), derivados de reacções de alcinóis com *trans*-$[\mathrm{FeBr_2}(\mathrm{depe})_2]$. Estudou-se (capítulo 2) a reactividade daqueles complexos a ataque nucleofílico, obtendo-se complexos de alcinilos neutros *trans*-$[\mathrm{FeBr}\{-\mathrm{C}\equiv\mathrm{C}-\mathrm{CPh_2(Nu)}\}(\mathrm{depe})_2]$ ($\mathrm{Nu^-}=\mathrm{H^-}$, $\mathrm{CN^-}$ ou $\mathrm{MeO^-}$), monocatiónicos *trans*-$[\mathrm{Fe(NCMe)}\{-\mathrm{C}\equiv\mathrm{C}-\mathrm{CPh_2(X)}\}(\mathrm{depe})_2]^+$ ($\mathrm{X}=\mathrm{NMe_2}$ ou NHMe) e dicatiónico *trans*-$[\mathrm{Fe(NCMe)}\{-\mathrm{C}\equiv\mathrm{C}-\mathrm{CPh_2(PMe_3)}\}(\mathrm{depe})_2]^{2+}$. No capítulo 3 prepararam-se complexos hidretos dinucleares, com pontes dinitrílicas, $[\{\mathrm{FeH(dppe)_2}\}_2(\mu\text{-}\mathrm{N}\equiv\mathrm{C}-\mathrm{X}-\mathrm{C}\equiv\mathrm{N})]^{2+}$ (X= CH=CH, $\mathrm{C_6H_4}$ ou $\mathrm{CH_2CH_2}$, dppe= $\mathrm{Ph_2PCH_2CH_2PPh_2}$), e diisonitrílicas, $[\{\mathrm{FeH(dppe)_2}\}_2(\mu\text{-}\mathrm{C}\equiv\mathrm{N}-\mathrm{X'}-\mathrm{N}\equiv\mathrm{C})]^{2+}$ ($\mathrm{X'}=\mathrm{C_6H_4}$ ou $\mathrm{C_6H_4-O-C_6H_4}$), e respectivos compostos mononucleares *trans*-$[\mathrm{FeH(N}\equiv\mathrm{C}-\mathrm{X}-\mathrm{C}\equiv\mathrm{N)(dppe)_2}][\mathrm{BF_4}]$ (X= CH=CH, $\mathrm{C_6H_4}$ ou $\mathrm{CH_2CH_2}$) e *trans*-$[\mathrm{FeH(C}\equiv\mathrm{N}-\mathrm{X'}-\mathrm{N}\equiv\mathrm{C)(dppe)_2}][\mathrm{BF_4}]$ ($\mathrm{X'}=\mathrm{C_6H_4}$ ou $\mathrm{C_6H_4-O-C_6H_4}$), por reacção dos correspondentes dinitrilos ou diisonitrilos com *trans*-$[\mathrm{FeHCl(dppe)_2}]$.

DETERMINAÇÃO DE CHUMBO, CÁDMIO E COBRE EM FOLHAS DE CHOUPOS (*POPULUS*) DE LISBOA POR VOLTAMETRIA DE REDISSOLUÇÃO ANÓDICA

Nelson Alberto Frade da Silva

Mestrado em Electroquímica Aplicada: *Engenharia Química*

Grau Concedido por: *Faculdade de Ciências da Univ. de Lisboa*

Orientadores:*Prof^a^. Doutora Maria Irene Lopes e Prof. Doutor Ruben A. E. Leitão*

Provas Concluídas em: *18 de Julho de 2003*

Neste trabalho apresentam-se os resultados de um estudo efectuado com vista à validação de um método voltamétrico (Voltametria de Redissolução Anódica de Onda Quadrada-SWASV) para determinação simultânea de quantidades vestigiais de metais tóxicos em amostras ambientais. A validação do método foi feita comparando os resultados obtidos por SWASV, com os obtidos por Espectrofotometria de Absorção Atómica com Câmara de Grafite (GFAAS). As amostras ambientais estudadas foram folhas de choupo recolhidas em vários locais de Lisboa entre os anos de 1999 e 2001. Estas foram sujeitas a um tratamento prévio de secagem e posterior digestão ácida num forno de microondas, comparando-se os resultados com os obtidos por digestão clássica. Para além da validação do método, procurou verificar-se se ocorreria uma diminuição do teor em chumbo atmosférico nas amostras, em consequência do desaparecimento da gasolina com chumbo do mercado em 1998. Estudou-se, paralelamente, a possibilidade de utilização de folhas de choupo como bioindicador. Em termos de validação da técnica, verificou-se uma concordância apreciável entre os resultados obtidos por SWASV e os obtidos por GFAAS, permitindo assim validar o método proposto. Em relação à variação da quantidade de chumbo presente nas folhas, foi observado que em qualquer dos locais investigados ocorreu, ao longo do tempo, uma diminuição do teor neste elemento. Esta diminuição foi directamente relacionada com o desaparecimento da gasolina com chumbo do mercado.

LIVROS

FENOMENOLOGIA DA COMBUSTÃO E EXTINTORES

A.M. Guerra, J.A. Coelho e R. Elvas Leitão

Edição: Escola Nacional de Bombeiros, ISBN:972-8792-01-8, Março 2003, pg.1-97.

A Fenomenologia da Combustão e Extintores aborda um tema de primordial importância para a formação de base do bombeiro. A correcta compreensão e aquisição de conhecimentos ao longo deste manual, exposto de uma forma simples, permitirá uma mais valia para qualquer bombeiro que posteriormente se deverá desenvolver e aperfeiçoar .

Para se entender o fenómeno do fogo, como reacção química particular acompanhada pela libertação de calor, é necessário conhecer a natureza da matéria, assim como, a sua constituição de base.

A matéria e as suas formas de ligação encontram-se intimamente ligadas ao seu estado físico e consequentemente ás suas características de combustível ou comburente. A conjunção destes dois factores com uma energia de activação e reacção em cadeia, permitem desenvolver ao longo do manual uma série de considerações, normalizações e definições, fundamentais para o entendimento deste fenómeno.

A classificação, características e funcionamento dos extintores, é uma das contribuições importantes para este manual, mas que de uma forma directa ou indirecta se encontram relacionadas com o estado físico do agente extintores e aspectos físico-químicos dos mesmos.

Neste manual estes conceitos básicos são apresentados ao longo do texto, pretendendo-se realçar aspectos mais científicos, assim como a utilização de normas portuguesas e europeias mais actualizadas.