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ISEL

NOTA INTRODUTÓRIA

O Conselho Científico do Instituto Superior de Engenharia de Lisboa (ISEL) dá a conhecer o trabalho científico desenvolvido por esta instituição no ano de 2005 e divulgado em fóruns nacionais e internacionais, através da 5.^a edição do Anuário Científico do ISEL.

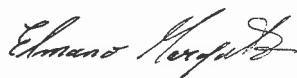
O ISEL tem sabido responder prontamente aos desafios de mudança que as sociedades modernas impõem, a atestá-lo estão a recente formação de todos os seus cursos ao modelo estabelecido pela Declaração de Bolonha e a criação de novos cursos em áreas emergentes do conhecimento.

Uma das maiores preocupações das escolas de engenharia na actualidade diz respeito à escassez de alunos. A algum excesso na oferta de vagas e de cursos de engenharia aliam-se a retracção do crescimento da população estudantil e a sua menor apetência por este tipo de formação superior, em especial nas áreas tradicionais. Este problema, que se estende a muitos outros países, faz apelo a uma reorganização do ensino da engenharia no nosso país. Tal reorganização terá de ser feita com rigor, no respeito pelas instituições, baseada em critérios objectivos avalizadores de competências e procurando a sua complementaridade.

O ISEL, consciente de que o cabal aproveitamento das suas competências só é possível no subsistema universitário, optou, em 2005, pela sua integração na Universidade de Lisboa (UL). Pensamos que a integração do ISEL na UL, para além de contribuir para a reorganização das escolas de engenharia na área metropolitana de Lisboa, é geradora de novas sinergias, das quais resultará, certamente, um melhor serviço por nós prestado.

Estamos convictos de que as opções tomadas são as que melhor servem os interesses do ISEL e do país, continuaremos a fomentar as acções conjuntas com a UL e a dar o nosso melhor contributo à sociedade através da formação de engenheiros qualificados e do incremento das actividades de investigação e desenvolvimento.

O Presidente do Conselho Científico



(Prof. Elmano Margato)



01

ENGENHARIA CIVIL

Anuário Científico 2005

ISEL

AValiação DO POTENCIAL DE REUTILIZAÇÃO DE EFLUENTES DE TRATAMENTO SECUNDÁRIO NA ZONA URBANA DA COVILHÃ COM RECURSO A FERRAMENTAS SIG. ESTUDO EXPERIMENTAL.

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A situação de seca verificada no biénio 2004/2005 limitou a disponibilidade de água na albufeira da Meimoa (origem de água que beneficiará o regadio do Bloco Covilhã-Fundão), cujo volume útil de armazenamento, em 2005, oscilou entre 8,9% e 27,8% do volume máximo previsto. Esta situação teve reflexos negativos, em especial na agricultura de sequeiro e nos sistemas de abastecimento de água potável. Por outro lado, a qualidade da água na albufeira da Meimoa apresentou-se variável, com evolução para o estado eutrófico nos meses de Julho a Setembro, tendo-se reflectido negativamente nas principais utilizações deste recurso hídrico. Nestes termos, a procura de origens alternativas de água, como a reutilização de ARUT, pode ajudar a colmatar as necessidades previstas, especialmente em períodos de escassez de água. A partir de quatro campanhas de amostragem, realizadas no ponto de descarga de uma ETAR com tratamento secundário, determinaram-se as características físico-químicas e microbiológicas do efluente final e avaliaram-se as possibilidades da sua reutilização, em especial na rega agrícola, tendo em atenção os requisitos da legislação e regulamentação vigentes e critérios de natureza técnica, ambiental e de protecção da saúde pública. Tratando-se de um estudo experimental, envolvendo reduzidos volumes de efluente, entendeu-se efectuar apenas o levantamento pormenorizado e georeferenciado de parcelas agrícolas localizadas em áreas próximas da ETAR e abrangidas pelo regadio do Bloco Covilhã-Fundão.

Com recurso a SIG, foi realizada uma análise exploratória dos dados recolhidos, que permitiu concluir que os cerca de 175 200 m³ de ARUT descarregadas anualmente num ponto da ribeira de Boidobra poderiam ser utilizados para a rega da totalidade das culturas classificadas na classe A ou para 30,9% das culturas da classe C, localizadas a uma distância máxima de cerca de 1,8 km. As características do efluente tratado não estavam, contudo, conformes com os requisitos definidos na legislação e regulamentação vigentes, o que pressupõe a necessidade de um tratamento de afinação para efeitos da sua reutilização ou descarga final. Porém, a norma portuguesa NP 4434 admite que um efluente com estas características possa ser utilizado em determinadas condições de controlo dos potenciais riscos sanitários. A utilização de ARUT para a rega de parcelas agrícolas apresenta-se, assim, como uma ferramenta de grande utilidade para a gestão sustentável da água na região da Cova da Beira, especialmente em situações de insuficiência de recursos hídricos.

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Livro de Resumos do 8º Congresso da Água, Associação Portuguesa de Recursos Hídricos, Figueira da Foz, Portugal, Março de 2005.

FUNDAÇÕES

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*Construção de
 empreendimentos na
 prática. Edições Verlag
 Dashofer, Janeiro de
 2005.*

A primeira parte de uma estrutura a ser construída são as suas fundações, que ficam em contacto directo com o terreno subjacente, e têm a importante função de lhe transmitir todo o peso da estrutura, assim como os esforços determinados pelas acções variáveis que sobre a mesma actuam. Tendo por base este princípio, a transferência de cargas da estrutura para o terreno subjacente deve efectuar-se sem que haja lugar a sobretensões, pois estas, provocando assentamentos excessivos ou roturas, podem originar danos à estrutura, pondo em risco o seu bom desempenho. Assim, a escolha adequada do tipo de fundação, o seu correcto dimensionamento e construção cuidada, são aspectos fundamentais na garantia da sua eficaz funcionalidade e da estabilidade da estrutura suportada. Tendo por base o exposto, no presente capítulo são abordados tópicos como:

- Requisitos gerais;
- Escolha do tipo de fundação;
- Tipos de fundações e campo de aplicação;
- Dimensionamento;
- Aspectos construtivos;
- Tipos de acidentes e patologias.

JUNTAS DE SOBREPOSIÇÃO DE REVESTIMENTOS DE IMPERMEABILIZAÇÃO DE COBERTURAS EM TERRAÇO

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O comportamento das juntas de sobreposição de revestimentos de impermeabilização nas coberturas em terraço é fundamental na qualidade do seu desempenho. Nesse sentido, o presente artigo pretende listar um conjunto de regras e procedimentos a adoptar na execução destas juntas em diferentes soluções de sistemas de impermeabilização.

Publicado em:

Revista Construção magazine, 2005, 12, 24-27.

INSTALAÇÃO DO SISTEMA DE IMPERMÉABILIZAÇÃO E DRENAGEM COM GEOSSINTÉTICOS EM TÚNEIS EM ESCAVAÇÃO

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Publicado em:
*Actas do 1º Seminário
português sobre
Geossintéticos, Porto
de 23 a 24 de
Novembro de 2005.*

Exigências de funcionalidade, longevidade e segurança, são algumas das muitas razões pelas quais se justifica a impermeabilização dos túneis em escavação. Nos últimos dez anos, a maioria dos túneis em escavação, construídos em Portugal, tem sido provida de sistemas de impermeabilização e drenagem associada à base de materiais geossintéticos, em que os principais, são as geomembranas de PVC e os geotêxteis de polipropileno. Este materiais permitem uma boa adaptabilidade aos mais variados tipos de suporte, são de instalação rápida, fiáveis e possuem uma boa relação – qualidade preço.

MIGRAÇÃO DE FLUIDOS ATRAVÉS DE ORIFÍCIOS NA GEOMEMBRANA

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A migração de fluidos através de orifícios na geomembrana foi estudada mediante a realização de ensaios laboratoriais. Para o efeito, simulou-se um sistema de confinamento de fundo de um aterro de resíduos, constituído por uma geomembrana com um orifício, um geossintético bentonítico (GCL) e uma camada de solo argiloso compactado (CCL). Mediu-se o fluxo na interface entre a geomembrana e o GCL e calculou-se a transmissividade da interface. Neste artigo apresentam-se os resultados de um estudo paramétrico realizado com o objectivo avaliar a influência de alguns dos aspectos que governam a migração de fluidos, nomeadamente a pré hidratação dos GCLs, a tensão confinante e a carga hidráulica. Os resultados sugerem que a pré-hidratação dos GCLs influencia a transmissividade de modo distinto, dependendo da tensão confinante aplicada. Sugerem, também, que o aumento da tensão confinante apenas afecta a transmissividade no caso dos GCLs pré hidratados. Por fim, o aumento da carga hidráulica não influenciou significativamente a transmissividade.

Publicado em:

Actas do 1º Seminário português sobre Geossintéticos, Porto de 23 a 24 de Novembro de 2005.

AVALIAÇÃO DA QUALIDADE DE APLICAÇÃO DE GEOMEMBRANAS EM ATERROS DE RESÍDUOS: O QUE DEVE MUDAR

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Publicado em:
*Actas do 1º Seminário
português sobre
Geossintéticos, Porto
de 23 a 24 de
Novembro de 2005.*

Nos aterros de resíduos, as geomembranas são utilizadas no sistema de confinamento basal e taludes, como barreira à fuga de lixiviados, sendo por isso essencial a manutenção da sua integridade física. Como a maioria dos defeitos na geomembrana ocorrem durante o processo de aplicação, é muito importante a identificação das actividades construtivas que podem por em causa a integridade das geomembranas e a detecção e reparação atempada dos danos efectuados. A usual implementação de um programa de garantia de qualidade de construção (PGQC) tem por objectivo assegurar a melhor eficiência do sistema de confinamento. Apesar da evolução nas tecnologias de realização de soldaduras e ensaios de monitorização, salvo raras excepções, os PGQC, no que se refere às geomembranas, têm permanecido praticamente inalterados durante a última década. Considerou-se por isso importante fazer uso da experiência acumulada, analisar a adequação dos métodos usualmente empregues na avaliação da qualidade de aplicação de geomembranas, compará-los com novas e comprovadas tecnologias e propor as alterações julgadas convenientes para melhorar a eficácia dos PGQC.

AS TIC NO ENSINO DA HIDRÁULICA DOS SISTEMAS ADUTORES

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Neste trabalho é apresentada a aplicação interactiva “Enchimento de adutores”, concebida para o ensino da hidráulica aplicada às condutas adutoras de sistemas de abastecimento de água. Desenvolvida em tecnologia Macromedia Flash MX, parte de uma abordagem eminentemente técnica e associa, em conformidade, o suporte científico necessário à análise da dinâmica dos fenómenos que lhe estão associados.

Publicado em:

*Actas da Conferência
Engenharia 2005,
Covilhã de 21 a 23 de
Novembro de 2005.*

O ENSAIO VIRTUAL DE CORTE DIRECTO

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Neste artigo são descritos os objectivos e a estrutura da aplicação interactiva subjacente à visualização de um ensaio virtual de corte directo, concebido para apoio à leccionação da disciplina de Mecânica dos Solos e Fundações 1 do Curso de Engenharia Civil do Instituto Superior de Engenharia de Lisboa, no âmbito do projecto de investigação “Ensino de Ciências da Engenharia Recorrendo às TIC”. Por fim são apresentadas algumas vantagens e limitações desta aplicação virtual.

Publicado em:

*Actas da Conferência
Engenharia 2005,
Covilhã de 21 a 23 de
Novembro de 2005.*

A QUÍMICA DO BETÃO

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Neste trabalho apresenta-se a aplicação interactiva “A Química em Concreto”, concebida para apoio ao processo de ensino/aprendizagem da química associada ao betão. Desenvolvida em tecnologia Macromedia Flash MX, recorre à representação virtual das estruturas cristalográficas dos compostos que constituem o betão como suporte à explicação científica das reacções químicas, inerentes à sua microestrutura e às condições a que está exposto, responsáveis pela sua resistência mecânica e durabilidade.

Publicado em:

*Actas da Conferência
Engenharia 2005,
Covilhã de 21 a 23 de
Novembro de 2005.*

MANAGEMENT OF BIOGAS FROM MUNICIPAL SOLID WASTE LANDFILLS TO CONVERT INTO ELECTRIC ENERGY

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The purpose of this paper is a contribution for a management information system to schedule the conversion of biogas from municipal solid waste landfills into electric energy, considering that the available biogas is constrained, not only at each conversion period, but also over the time horizon. The management of biogas from municipal solid waste landfills to convert into electric energy has to face the nowadays profit environment, considering how to make the best present profit, consuming biogas to convert into electric energy, without compromising future potential profit. We present an approach based on a nonlinear programming problem to support the optimal decision management of electric energy production in municipal solid waste landfills. A case study is provided to show the capabilities of this approach and its adequacy.

Publicado em:

*Proceedings of 1st
International
Conference on
Electrical Engineering
(CEE'05), Coimbra, 10
a 12 de Outubro de
2005.*

APROVEITAMENTO ENERGÉTICO DO METANO DA BIOMASSA DOS ATERROS SANITÁRIOS: GESTÃO DE CURTO-PRAZO

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Em Portugal nos últimos 10 anos houve uma grande mudança na política de gestão de resíduos sólidos urbanos (RSU), tendo-se encerrado e recuperado cerca de 341 lixeiras existentes e construído em sua substituição 37 aterros sanitários. Uma nova etapa está agora em pleno desenvolvimento com objectivos e metas fixadas pela União Europeia, no que se refere à redução da produção de RSU, aumento da recolha selectiva, reutilização, reciclagem e valorização orgânica e energética dos resíduos produzidos. Paralelamente, a União Europeia estabeleceu também metas de redução global para a emissão de gases com efeito de estufa e para o aumento do uso de fontes de energia renováveis alternativas. Neste contexto, uma das fontes de energia renovável que no nosso país começa a ser aproveitada para produção de energia eléctrica é o biogás, proveniente da decomposição anaeróbia dos RSU depositados em aterro, conseguindo-se simultaneamente atingir dois objectivos: diminuir a emissão de metano para a atmosfera, através da queima do biogás dos aterros, conforme obriga o Decreto-Lei nº 152/2002 de 23 de Maio e contribuir para a valorização energética dos resíduos. Assim, para além de se cumprir a legislação em vigor, o aproveitamento do biogás para produção de energia eléctrica constitui uma mais valia para as empresas concessionárias das unidades de tratamento e destino final dos resíduos, por esta fonte de energia alternativa poder proporcionar não só uma autosuficiência em energia eléctrica dessas unidades, mas também a exportação da energia excedentária para a Rede Eléctrica Nacional, concorrendo dessa forma para a gestão auto-sustentada que se pretende para essas infraestruturas. Esta comunicação pretende contribuir para a optimização da gestão da energia eléctrica obtida a partir da queima do biogás. No segundo ponto é apresentado o formalismo para uma aplicação informática que simula o comportamento técnico-económico da Gestão de Curto-Prazo do biogás para a conversão de energia eléctrica, sendo o modelo matemático formulado como um problema de programação matemática com restrições. No terceiro ponto é apresentada uma simulação para um caso de estudo de Gestão de Curto-Prazo. No último ponto, são apresentadas as principais conclusões..

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Relatório LNEC
nº 206/04-NP, LNEC,
Lisboa, Março de
2004.

SANTO TIRSO SANITARY LANDFILL: STUDY OF WASTE PROPERTIES

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Waste characterization is critical in planning, design, and operation of solid waste management systems. Since solid waste and the materials derived there from are, in many situations, difficult to sample and analyze, the assessment of waste characteristics requires that proper and reliable methods and procedures be used to determine the values of the characteristics. The study reported herein was conducted to characterize the solid wastes being disposed up to now at Santo Tirso landfill, since 1995.

Publicado em:

*Proceedings of
International
Workshop hydro
physico mechanics of
landfills, Grenoble,
França, 21 e 22 de
Março de 2005*

NOVO MODELO DE ENSINO DE MATEMÁTICA EM ENGENHARIA

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O ensino baseado apenas numa estrutura logicamente coerente que normalmente se inicia com a apresentação formal de axiomas, seguida por teoremas e terminando algumas aplicações matemáticas dos conceitos, permite uma boa planificação da estrutura do curso, normalmente baseada na apresentação expositiva dos assuntos, cobrindo todos os temas relevantes. No entanto esta metodologia tem a desvantagem de ser inflexível na adaptação aos modos de ser e de pensar de cada aluno.

Na maioria dos alunos, este sistema de ensino apenas produz uma aprendizagem centrada na memorização de umas quantas fórmulas, e procedimentos, a serem esquecidos após os exames. É neste contexto que se torna importante a busca de alternativas didáticas. Uma das fontes para procurar ideias sobre como melhorar a compreensão dos alunos é o entendimento de como é produzido o conhecimento matemático.

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E-ciência Magazine, nº23, Especial Ensino da Matemática em Portugal, Abril 2005

INTERPRETAÇÃO ALGÉBRICA DO MÉTODO DOS MÍNIMOS QUADRADOS

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Publicado em:
*Científica – Newsletter
da Texas Instruments,
Fall 2005.*

O método dos mínimos quadrados é uma técnica, muito difundida, para o cálculo de estimativas de parâmetros e de ajuste de dados. É um das técnicas mais antigas da estatística moderna e foi divulgada em 1805, pelo matemático francês Legendre (1752-1833). No entanto constatou-se que este método é mais antigo. Depois da publicação de Legendre, o famoso Matemático alemão, Gauss (1777-1855), publicou em 1809 um trabalho (*Theoria motus corporum coelestium in sectionibus conicis Solem ambientium*), onde reclamava para si a descoberta prévia deste método, tendo-o desenvolvido em 1795. Actualmente, o método dos mínimos quadrados é usado para determinar ou calcular os valores numéricos dos parâmetros para ajustar uma função a uma colecção de dados e caracterizar as propriedades estatísticas de estimativas. Esta técnica sofreu evoluções, dando origem a técnicas mais complexas, tais como os Métodos de Projecção, ou o Método dos Mínimos Quadrados Ponderados, constituindo um processo de cálculo para corrigir metodicamente resultados experimentais ou de medições, com vista à obtenção do seu valor mais provável.

O ENSINO DA MATEMÁTICA ASSISTIDO POR COMPUTADOR NUM CURSO DE ENGENHARIA

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Com esta comunicação apresentámos o projecto 2AMAC – Apoio na Aprendizagem de Matemática Assistido por Computador – no contexto do ensino da Matemática no curso de Engenharia Civil no ISEL. Mostrámos, também, de que forma este projecto contribui para uma melhoria da qualidade de ensino nas disciplinas de Análise Matemática I e Análise Matemática II do curso de Engenharia Civil, recorrendo à utilização de tecnologias de e-Learning/b-Learning, considerando as especificidades próprias para o Ensino Superior, utilizando uma abordagem diferenciada das abordagens comuns ao problema do e-Learning.

Publicado em:
*VI PMATE-
Universidade de
Aveiro.*

INTRODUÇÃO AO MÉTODO DOS ELEMENTOS FINITOS

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Publicado em:
*Departamento de
Matemática –
Universidade de
Aveiro, Outubro 2005*

Com esta introdução aos elementos finitos pretendemos apresentar as noções básicas e fundamentais deste método, tanto do ponto de vista teórico (existência e unicidade da solução, convergência), como prático (cálculo explícito de uma aproximação com um computador). Mostramos neste documento o processo completo de implementação que vai desde a modelação matemática de um problema real até à resolução numérica do problema aproximado. Podemos dividir este processo nas etapas: de modelação do problema em equações (capítulo 1); de estudo teórico das equações (capítulos 3 e 7), da discretização das equações e o estudo dos métodos numéricos (capítulos 4 e 8) e finalmente o cálculo explícito de uma aproximação (capítulo 5 e 9). Neste manual, introduzimos as ferramentas usuais dos elementos finitos: problema variacional, teorema de Lax-Milgram e de Lions, princípio do máximo, espaço de discretização finito, os esquemas em espaço e tempo, a estabilidade dos métodos e ordens de convergência do método.

USE OF AMBIENT VIBRATION TESTS FOR STRUCTURAL IDENTIFICATION: 3 CASES STUDY

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In this study we summarize the results of Ambient Vibration Testing on 3 different structures: the Portuguese Telecom Tower; the Cabril concrete dam; and the “nuns” church a masonry structure in Lagos, south Portugal. In the three cases Finite Element Models of the structures were built and the models were updated with results of Ambient Vibration Tests.

These studies were financially supported by Dynaseis – FCT36071 ECM 2000; Caravela – IPL 50/2003. The study performed at Cabril dam was technically supported by Laboratório Nacional de Engenharia Civil.

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*Proceedings do 1st
IOMAC (International
Operational Modal
Analysis Conference),
realizado em
Copenhaga na
Dinamarca, Abril de
2005.*

STRUCTURAL AND DYNAMIC ANALYSIS OF N. SR.^a DO CARMO CHURCH, LAGOS, PORTUGAL

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Publicado em:
*Proceedings do VIst
EURODYN (European
Conference on
Structural Dynamics),
realizado em Paris na
França, Setembro de
2005.*

In this paper we present the structural diagnosis and the dynamic analysis, evaluation of natural frequencies and mode shapes, of N. Sra. do Carmo church, built in the 16th century, destroyed by the 1755 Lisbon earthquake and partially rebuilt afterwards. The church is part of the cultural heritage of the city of Lagos. Experimental data is obtained through ambient vibration testing (AVT) and a Finite Element Model (FEM) of the structure is presented. The main purpose of this study is the evaluation of the structural behavior due to the presence of a longitudinal crack along the vault that covers the central nave. This work was developed in the framework of project CARAVELA - Instituto Politécnico de Lisboa.

RESTAURO E RECONSTRUÇÃO DE SANCAS, MOLDURAS E FLÔRÕES EM ESTUQUE TRADICIONAL

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2 Laboratório Nacional de Engenharia Civil

3 Instituto Superior Técnico

Nas intervenções realizadas nos edifícios antigos, considera-se que, sempre que possível, se deve optar por soluções tradicionais, quer no que diz respeito à manutenção de elementos semelhantes aos existentes, quer quanto à utilização de técnicas testadas.

Os elementos decorativos executados em estuque tradicional, frequentes nos edifícios antigos, constituem muitas vezes verdadeiras obras de arte, que interessa manter e preservar. Neste âmbito, interessa conhecer não só os materiais mas também os processos construtivos tradicionais, com algumas adaptações actualizadas.

O presente artigo pretende por isso fornecer um contributo para o restauro ou reconstrução de alguns dos mais artísticos elementos estucados presentes nos edifícios antigos, como sejam as sancas, molduras, cimalthas, meias colunas, florões, cornijas ou mísulas.

O artigo começa por referir os materiais utilizados nas pastas e argamassas dos elementos estucados, como sejam o gesso, a quantidade de água de amassadura, os retardadores de presa, a cal aérea e as cargas minerais. Indica-se depois o processo de execução dos elementos de secção constante, moldados *in situ* ou em bancada e, por fim, a modelação de peças por *fusão*, em moldes de peça única ou por *tacelos*.

Publicado em:

Revista Património Estudos, n.º 8, Ministério da Cultura/IPPAP, Lisboa, Novembro de 2005.

A SURVEY ON ASSET ALLOCATION IN THE PORTUGUESE REAL ESTATE MARKET

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Publicado em:
International Conference "CIB-INFORMATION AND KNOWLEDGE MANAGEMENT IN A GLOBAL ECONOMY: Challenges and Opportunities for Construction Organizations", May 2005, IST, Lisbon (pp.677-686).

Most important academic theoretical developments in finance and investment have been transferred to widespread practical use, especially in the more efficient securities markets. Real estate investment research has followed these developments, with a lag of about 20 years, but to some extent, common practice of asset allocation in a property portfolio still relies a lot on a qualitative and subjective personal judgment.

To assess the reality and extent of this situation among the institutional property investors operating in the Portuguese market, a study based on a survey among a reference group of managers of large real estate portfolios was developed. This includes real estate fund management societies, pension funds and significant real property investment companies. The survey covers management decision-making practices, use of specific information, indices and databases, the role of appraisal, and the use of quantitative models regarding performance measurement, benchmarking and optimization of asset allocation. The aim is to establish the real gap between theory and practice. Research design is presented and justified against economic reality, and recent related and similar studies.

CARACTERÍSTICAS DAS MEMBRANAS DE IMPERMEABILIZAÇÃO

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- 3 Investigador Coordenador. LNEC, Lisboa - Portugal
- 4 Professora Coordenadora. ISEL, Lisboa - Portugal

O revestimento de impermeabilização é entendido como o conjunto de todos os materiais, componentes e acessórios essenciais para munir a cobertura de uma barreira estanque à água que sobre ele estacione ou circule. No entanto, o revestimento de impermeabilização deve ainda ter outras características fundamentais, como a capacidade de se deformar sem rotura ou fissuração ao longo da sua vida útil, nas condições de exposição previstas, tanto sob a acção das sucções do vento, como acompanhando os eventuais movimentos do seu suporte. Uma incorrecta selecção da membrana de impermeabilização pode conduzir à ocorrência de problemas nas coberturas e nos próprios edifícios, por não desempenharem correctamente a sua função. Desses problemas resultam quase sempre infiltrações de água para as camadas subjacentes à do revestimento de impermeabilização ou para os espaços do último piso, provocando prejuízos que podem ser significativos. Assim, foi objectivo deste artigo indicar as principais características das membranas a integrar nos sistemas de impermeabilização de coberturas em terraço.

Publicado em:

Revista Engenharia Civil, Escola de Engenharia da Universidade do Minho, n.º22, Guimarães, Janeiro 2005, páginas 59-71.

MADEIRA NA CONSTRUÇÃO CIVIL: A OPÇÃO AMBIENTALMENTE CORRECTA

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Publicado em:
*1st International
Congress Energy and
Environment
Engineering and
Management, Instituto
Politécnico de
Portalegre, 18 a 20
Maio 2005.*

Sendo o sector da construção civil, um dos principais consumidores de recursos energéticos ao nível dos países industrializados, será consequentemente ele, um dos sectores com maiores responsabilidades na urgente busca de alternativas que anulem ou minimizem a crescente espiral de consumo e poluição ambiental em que actualmente nos encontramos.

Hoje em dia, a indústria da construção é considerada a que mais contribui para a delapidação dos recursos naturais, para o consumo de energia, para a poluição do ar e para a criação de resíduos.

O material madeira e seus produtos derivados, surgem então como resposta eficaz a essa preocupação. Os principais objectivos da presente comunicação, localizam-se ao nível da apresentação do uso da madeira como o material de construção civil mais eco-eficiente e o que mais contribui para a sustentabilidade do desenvolvimento a nível global, contextualizando-o na actual panorâmica da construção em Portugal e discretizando as suas características, potencialidades e tipos de aplicação.

EVALUATION OF THE 1755 EARTHQUAKE SOURCE USING TSUNAMI MODELING

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The tsunami generated by the 1755.11.01 earthquake is the biggest known event in SW Europe. However, the precise location of its main shock is still a matter of debate, mainly because up to the present, no candidate source has been able to justify seismic and tsunami descriptions in a satisfactory way. Tsunami modelling has proved to be an important tool to evaluate candidate sources, in such cases where a considerable number of good quality observations exist: wave heights, travel times, polarity of the first movement, and interval between successive flux/reflux movements. The tsunami that followed the earthquake was observed all over the north Atlantic coasts from Cornwall (uk) to north morocco; significant run up heights were also reported from the west Indies. This paper presents a comparison of different sources, from the tsunami point of view. We focus on the following candidate sources: (1) Marquis de Pombal/Guadalquivir pop-up; (2) Gibraltar slab. The test of the source is achieved through numerical modelling of the tsunami all over the north Atlantic area. The results presented incorporate historical observation along the European coasts and Western Indies.

Publicado em:

250TH ANNIVERSARY
OF THE 1755 LISBON
EARTHQUAKE

TSUNAMIS IN PORTUGAL - NUMERICAL SIMULATION OF THE 26.05.1975 GLORIA FAULT TSUNAMI

**Soares, Pedro M.M.^{1,2}; Baptista, M.A.^{1,2};
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The Portuguese mainland coast has been affected by moderate and strong submarine earthquakes that generated tsunamis. The most significant is the well know Lisbon event generated by the 8.75 earthquake that devastated the Iberian Peninsula. Along the Azores coast several tsunamis have been reported: 1522, 1614, 1757 and 1837. Although not very frequent along the Portuguese coasts the social and economic impact of great tsunamis is nowadays greatly amplified by the existent urban concentration near coastal areas in Portugal, mainland and Azores. The 26 May 1975 earthquake of $M_s=7.9$ magnitude, with epicentre located in the North Atlantic south of Gloria Fault, produced a tsunami detected in the coastal tide stations of Portugal mainland, Azores and Cadiz in Spain. In this paper we evaluate the tsunami source, using an elastic half-space model and we compute the synthetic tsunami propagation, using a non linear shallow water model. Synthetic results are compared with mareograms for travel times, amplitudes and periods, and the tsunami source is compared with the seismic source.

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*Geophysical Research
Abstracts, Vol. 7,
09870, 2005
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7962/gr/EGU05-A-
09870
© European
Geosciences Union
2005*

COMMENT ON “LISBON 1755: A CASE OF TRIGGERED ONSHORE RUPTURE?” BY SUSANA P. VILANOVA, CATARINA F. NUNES, AND JOAO F.B.D. FONSECA

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The work published recently by Vilanova et al. (2003) in the Bulletin of the Seismological Society of America proposes that the accounts of destruction and other effects reported in the Lisbon area as a result of the 1 November 1755 earthquake are best explained by a local rupture on the Lower Tagus Valley fault (LTVF), triggered by the static stress change produced by the main offshore source located in the Gorringe area. Because of the potential impact of this hypothesis on the seismic hazard of the Lisbon area, we discuss and complement the evidence presented by Vilanova and co-workers, concluding that the “local rupture model” should remain, for the moment, as an unsubstantiated speculation.

Publicado em:

*Bulletin of the
Seismological Society
of America, Vol. 95,
No. 6, pp. 2534–2538,
December 2005, doi:
10.1785/0120040023*

USE OF AMBIENT VIBRATION TESTS FOR STRUCTURAL IDENTIFICATION: 3 CASES STUDIES

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In this study we summarize the results of Ambient Vibration Testing on 3 different structures: the Portuguese Telecom Tower; the Cabril concrete dam; and the “nuns” church a masonry structure in Lagos, south Portugal.

Ambient vibration testing was conducted in order to determine natural frequencies, mode shapes and damping ratios. An Finite Element Model updating of each structure was developed and updated with experimental results. The experimental results and the analytical results are presented, in this paper, and compared.

These studies were financially supported by Dynaseis – FCT36071 ECM 2000; Caravela – IPL 50/2003. The study performed at Cabril dam was technically supported by Laboratório Nacional de Engenharia de Civil do cromóforo, por retroação metal-ligando.

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*Livro de Resumos da
1st IOMAC-
International Output
Modal Analysis,
Copenhagen, Denmark*

STRUCTURAL AND DYNAMIC ANALYSIS OF N. SRA. DO CARMO CHURCH, LAGOS PORTUGAL

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Lagomarsino, S.²; Costa, J.P.³**

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In this paper we present the structural diagnosis, the dynamic analysis, evaluation of natural frequencies and mode shapes, of N. Sra. do Carmo church, built in the 16th century, destroyed by the 1755 Lisbon earthquake and partially rebuilt afterwards. The church is part of the cultural heritage of the city of Lagos. Experimental data is obtained through ambient vibration testing (AVT) and a Finite Element Model (FEM) of the structure is presented. The main purpose of this study is the evaluation of the structural behavior due to the presence of a longitudinal crack along the vault that covers the central nave. This work was developed in the framework of project CARAVELA - Instituto Politécnico de Lisboa.

Publicado em:

*Livro de Resumos da
Conferência Eurodyn,
Paris, França,
Setembro 2005*

SUMATRA E KATRINA: DESASTRES ANUNCIADOS

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2 Departamento de Engenharia Civil ISEL, Lisboa, Portugal

Publicado em:
Engenharia e Vida, pp
42-44, Out 2005.

Duzentos e cinquenta anos após a primeira catástrofe natural percebida a nível global - o sismo e o tsunami de 1 de Novembro de 1755 - os grandes desastres continuam a causar perplexidade. Apesar do impacto que teve no pensamento europeu do século XVIII, as reacções a este tipo de eventos serão hoje em dia diferentes? Actualmente os grandes desastres naturais continuam a surpreender quer pelo seu impacto quer pela reacção sempre imprevisível como a humanidade encarar a sua relação com a natureza.

ATTENUATION OF SEISMIC INTENSITY IN SW PORTUGAL-IBERIA: RECONCILING HISTORICAL AND INSTRUMENTAL DATA

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2 Centro Geofísica Univ. de Lisboa

3 Univ. do Algarve

There is a growing need for quantitative seismic hazard estimations that can be used in SW Portugal as a basic tool for territorial management. These estimations rely strongly on well-constrained attenuation models which, in a region of moderate seismicity must be based on a mix of instrumental and historical studies. In this study we re-evaluated the attenuation of Medvedev, Sponheuer and Karnik (MSK) intensities for the larger and best known historical earthquakes in Portugal. These events cover a range of magnitudes between 6.0 and 8.7 and epicentral distances up to several hundreds of km. We combined this information with instrumental data available for small magnitude earthquakes (2.9 to 4.8) and epicentral distances between 40km and 400km, into a single empirical attenuation model. This model represents an improvement with regard to hazard studies because it reproduces well existing observations in terms of magnitudes and epicentral distances and also contributes to more accurate quantitative hazard estimations in SW Portugal and SW Iberia.

Publicado em:

Eos Trans. AGU,
86(52), Fall Meet.
Suppl.

MODELING THE DIURNAL CYCLE OF THE SUMMER BOUNDARY LAYER: THE CICLUS EXPERIMENT

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Improvements in the representation of turbulence and convection in the dry boundary layer require detailed comparisons between observations and numerical results. Here, a case taken from the CICLUS field experiment in 1998, is used to assess the performance of two mesoscale models and to discuss possible improvements in their parametrizations. Problems found in the results with the standard version of the US Navy COAMPS model, associated with an largely insufficient boundary layer development, have been significantly alleviated with the implementation of modified diagnostic for the mixing length, recently proposed by Teixeira and Cheinet. Simulations of the same case with the research model MesoNH, reveal a much better in its standard version. Possible improvements in the detailed boundary layer structure are sought, through the implementation of the new EDMF parameterization scheme.

Publicado em:

*Proceedings do
6^o Encontro Luso-
Espanhol de
Meteorologia, 2005,
126-131. (Extended
Abstract)*

A NEW PARAMETRIZATION SCHEME FOR THE CLEAR AND CLOUDY BOUNDARY LAYER

Soares, P.M.M.^{1,2}; Miranda, P.M.A.²; Teixeira, J.³; Siebesma, A.P.⁴; Cardoso, S.²

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The recently proposed Eddy-Diffusivity Mass-Flux parameterization scheme is here tested in a number of case studies in 1D and 3D settings. The scheme incorporates, in an integrated approach, the usual eddy-diffusivity closure and the mass-flux concept developed for cloud convection. Due to its integrated nature, the new parameterization avoids the need to switch between the two schemes. At the same time it allows for the benefits of the mass-flux approach to the representation of dry convection and, in cloudy conditions, guarantees consistence in the fluxes between the sub cloud and cloud layers. Initially developed within the MesoNH research model the scheme is now being tested in the ECMWF model.

Publicado em:

*Proceedings do
6º Encontro Luso-
-Espanhol de
Meteorologia, 2005,
277-282. (Extended
Abstract)*

MODELING THE SUMMER DIURNAL CYCLE IN THE SW IBERIA, THE CICLUS EXPERIMENT

Soares, P.M.M.^{1,2}; Miranda, P.M.A.²; Teixeira, J.³; Siebesma, A.P.⁴; Ferreira, J.P.⁵

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*In combined Preprints
of the Sixth
Conference on Coastal
Atmospheric and
Oceanic Prediction
Processes (85th
American
Meteorological Society
Annual Meeting),
2005, P2.5, 1-7.
(Extended Abstract)*

Observations from the CICLUS experiment (Climate Impact of Changes in Land Use), performed in Southern Portugal in 1997-99, are compared against boundary layer and mesoscale simulations with two non-hydrostatic models. The study focus on two days of intensive observations, with 3 hourly radiosondes in clear sky conditions, when the regional atmospheric circulation is dominated by a Heat Low type atmospheric circulation associate with the sea breeze cycle in the Iberian Peninsula. Surprisingly, the standard version of the COAMPS model fails to reproduce the observed boundary layer diurnal cycle, producing insufficient growth. Results are much improved with a new mixing length formation (Teixeira & Cheinet 2003, Teixeira et al 2004). A more substantial change of the PBL scheme, using a new Eddy-Diffusivity/Mass-Flux approach (Siebesma & Teixeira 2000, Soares et al 2004) is also tested. An analysis of the mesoscale circulation in the region indicates that the vertical profiles of specific humidity, characterized by a persistent and very dry layer just above the boundary layer top inversion, are related with the interaction between a low level cyclonic (heat low) circulation and the prevailing anticyclonic flow aloft.

THE EDMF SCHEME RESULTS FOR SHALLOW CUMULUS CONVECTION CASES

Soares, P.M.M.^{1,2}; Miranda, P.M.A.²; Teixeira, J.³; Siebesma, A.P.⁴; Catarino, A.²

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The eddy-diffusivity/mass-flux (EDMF) parameterization was proposed to describe both the clear and the shallow cumulus boundary layer. The EDMF scheme is based on scale decomposition between small scale turbulence, described by eddy-diffusivity, and updrafts, described by mass-flux. Two different formulations were developed. For Global Circulation Models the EDMF scheme is essentially based on well known boundary layer equations, and presented remarkably good results in a clear convective boundary layer case. For Limited Area models the EDMF parameterization is based on the turbulent kinetic energy equation. The results obtained with the MesoNH model, where the different schemes are implemented, and show improvements in the representation of the convective boundary layer, with and without cumulus.

In this paper an evaluation of the EDMF results for the ARM case, corresponding to a diurnal cycle of cumulus convection, and for the BOMEX case is made. The cloud base mass-flux closure and the momentum vertical transport issues are specially addressed. The results are compared against Large Eddy Simulation data.

Publicado em:

Revista do Centro de Ciências Naturais e Exactas (UFESM-Brasil), 337, Dezembro de 2005.

CLEAR AND CLOUDY BOUNDARY LAYER IN SOUTHERN PORTUGAL: EDMF RESULTS

Soares, P.M.M.^{1,2}; Miranda, P.M.A.²; Teixeira, J.³; Siebesma, A.P.⁴

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Publicado em:
*Geophysical Research
 Abstracts of the
 European Geosciences
 Union, Vol. 7, 09924,
 Viena, Áustria, Abril
 de 2005.*

The recently proposed Eddy-Diffusivity Mass-Flux parametrization scheme is here tested against 3D case studies of clear and cumulus boundary layers. This turbulence/convection scheme combines the usual eddy-diffusivity closure and the mass-flux concept. Due to its integrated nature, the parametrization avoids the need to switch between the two schemes in the case of cloudy convective boundary layer. At the same time, it allows for the benefits of the mass-flux approach to the representation of dry convection and, in cloudy conditions, guarantees consistency in the fluxes between the sub-cloud and cloud layers.

Previously, the EDMF scheme was evaluated in the 1D framework, using LES results, as those of the Nieuwstadt and the ARM cases. For both the dry and the shallow cumulus boundary layer the scheme presented important improvements in the representation on the mean boundary layer properties and cloud variables.

The CICLUS field experiment (Climate Impact of Changes in Land Use) was performed in Southern Portugal in 1997-99 to better characterise the atmospheric circulations in the region. The Southern Portuguese coast is a rather interesting case for the study of boundary layer processes, due to a complex pattern of surface heating.

Two cases taken from the CICLUS experiment are used to evaluate the performance of the MesoNH model, where the EDMF scheme is implemented. The first study focus on two days of intensive observations, with 3 hourly radiosondes in clear sky conditions, when the regional atmospheric circulation is dominated by a Heat Low associated with the sea breeze in the Iberian Peninsula. A shallow cumulus diurnal cycle is considered to discuss how the new scheme improves the description of the complex interaction between the regional thermal circulations and the cumulus cloud pattern.

TSUNAMIS IN PORTUGAL - NUMERICAL SIMULATION OF THE 26.05.1975 GLORIA FAULT TSUNAMI

Soares, P.M.M.^{1,2}; Baptista, M.A.^{1,2};
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The Portuguese mainland coast has been affected by moderate and strong submarine earthquakes that generated tsunamis. The most significant is the well know Lisbon event generated by the 8.75 earthquake that devastated the Iberian Peninsula.

Along the Azores coast several tsunamis have been reported: 1522, 1614, 1757 and 1837. Although not very frequent along the Portuguese coasts the social and economic impact of great tsunamis is nowadays greatly amplified by the existent urban concentration near coastal areas in Portugal, mainland and Azores. The 26 May 1975 earthquake of $M_s = 7.9$ magnitude, with epicentre located in the North Atlantic south of Gloria Fault, produced a tsunami detected in the coastal tide stations of Portugal mainland, Azores and Cadiz in Spain.

In this paper we evaluate the tsunami source, using an elastic half-space model and we compute the synthetic tsunami propagation, using a non linear shallow water model. Synthetic results are compared with mareograms for travel times, amplitudes and periods, and the tsunami source is compared with the seismic source.

Publicado em:

*Geophysical Research
Abstracts of the
European Geosciences
Union, Vol. 7, 09870,
Viena, Áustria, Abril
de 2005.*

NUMERICAL SIMULATION OF BOUNDARY LAYER CLOUDS

Soares, P.M.M.^{1,2}; Miranda, P.M.A.²; Catarino, A.²

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Publicado em:
*Proceedings of the 5th
Annual Meeting of the
European
Meteorological
Society, EMS05-A-
00252, Utrecht,
Holanda, Setembro de
2005.*

The onset and dissipation of fog in stable boundary layers is often difficult to predict with simple single column models, due to the effects of advection, turbulence and microphysical processes. However, some state-of-the-art mesoscale models include sophisticated parameterizations that may capture the main features of those processes.

In this study we simulate a few fog events with an LES model and the MesoNH mesoscale model, and compute diagnostics of cloud formation and dissipation processes.

TABELAS TÉCNICAS

**Correia dos Reis, A.; Farinha, M. Brazão;
Farinha, J.P. Brazão**

Departamento de Engenharia Civil, ISEL, Lisboa, Portugal

O livro "Tabelas Técnicas" foi inicialmente publicado o título "Tabelas de Resistência de Materiais", com duas edições em 1926 e 1937, tendo-lhe sucedido, a partir de 1942, o livro com a designação actual de "Tabelas Técnicas", com uma primeira fase de oito edições, a última das quais em 1977, dirigida pelo Eng. J. S. Brazão Farinha. Após um interregno de 15 anos seguiram-se, em segunda fase, as edições de 1992, 1993, 1995, 1998, 2000, 2003 e 2005 com colaboração do Eng. A. Correia dos Reis, envolvendo sucessivas actualizações, reajustamentos e ampliações. Consideram os autores que, pela sua própria natureza esta é uma publicação técnica fundamental que deve estar sujeita a permanente evolução e actualização, por períodos não superiores a três anos.

A intensa publicação de normas tem implicado a progressiva supressão de alguns elementos e a inclusão de outros. O desenvolvimento da electrónica, em particular a partir da década de 80 do século XX, implicou uma total revisão nos métodos e sobretudo no modo de encarar a resolução dos problemas matemáticos; o alargamento da aplicação directa dos conceitos fundamentais - em que a complexidade algébrica deixou de ter importância para a resolução de muitos problemas práticos de engenharia - impôs o desenvolvimento do capítulo respeitante à Matemática.

Na edição de 2003 incluem-se textos novos sobre catenárias, fundações circulares, equipamento de sondagem, protecção de incêndios em construções metálicas, um capítulo sobre projectos, e alguns pormenores.

Foi retirado o capítulo de materiais de construção a incluir e ampliar no livro novo Organização e Gestão de Obras.

Publicado em:
Edições Técnicas
E.T.L., Lda.; Janeiro de
2005

CONSTRUÇÃO DE EMPREENHIMENTOS NA PRÁTICA

**Farinha, M. Brazão; Lauria, A.; Pinto, A.;
Lopes, M. Alfaro; Cabrita da Palma, J.; Portugal, J.;
Guimarães, J.; Brás, M.; Ferreira, M.; Nogueira, R.M.**

Departamento de Engenharia Civil, ISEL, Lisboa, Portugal

Publicado em:
Verlag Dashöfer;
Janeiro de 2005

O presente livro foi publicado como manual destinado à aplicação e desenvolvimento de processos e métodos da construção, nomeadamente de edifícios.

O livro está dividido em catorze capítulos:

- Informações gerais
- Estaleiro e trabalhos e preparação
- Demolições, contenção e movimentos de terras
- Fundações
- Estruturas de Betão Armado
- Alvenarias, vãos interiores e exteriores
- Coberturas em edifícios e sua impermeabilização
- Instalações de águas e esgotos
- Instalações eléctricas e de telefones
- Instalações de gás
- Instalações de aquecimento, ventilação e ar condicionado
- Instalações de ascensores e de monta-cargas
- Revestimentos e acabamentos
- Arranjos exteriores

AMS AND PALEOMAGNETIC VARIATIONS ALONG SECTIONS CROSS-CUTTING FOUM ZGUID DYKES AND SEDIMENTARY HOST ROCKS: IMPLICATIONS FOR THE FLOW AND PROPAGATION OF MAGMA

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Understanding the flow and propagation of magma using rock magnetic analyses along planar and sub-vertical intrusive bodies as function of its thicknesses is the aim of this study. Rock magnetism, anisotropy of magnetic susceptibility and paleomagnetism studies were applied to samples collected along several sections cross-cutting the Jurassic dykes of Fom-Zguid and sedimentary host rocks (Southern Morocco). For the igneous rocks, titanomagnetite Ti-low is the main magnetic carrier. Petrographic analysis show that the main Ti phase (ilmenite) occurs either as lamellae within spinel (center of the dyke) or as isolated grains (dyke margin). For sedimentary host rocks the magnetic signal is mainly carried by hematite for domains near the contact and by hematite and magnetite for domains farther located. Hematite content reflects the Fe-metasomatism intensity experienced by the sedimentary rocks, traduced by a decrease of the hematite dissemination intensity with distance from the dykes margins.

The magnetic fabric of the dykes and host-rocks shows different magnetic fabrics patterns according to the contact distance. For samples of the dykes nearest the margins the magnetic foliation systematically shows a direction sub-parallel to the dykes plane, plunging sub-vertical or towards the core of the dyke. As the distance to the margins increase, the magnetic foliation systematically displays: i) increase of the imbrication angle, with clockwise rotation at the NW margins and anti-clockwise rotation at the SE margins; and, ii) inversion of the plunge direction, now, dipping towards the respective margins. Concerning the sedimentary host rocks, with the approach to the dykes margins, we verify a transition from a sub-horizontal magnetic foliation to one plunging towards the contact margins. This transition is accompanied by the paleomagnetic results, changing progressively along a direction perpendicular to the dykes trend.

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International
Association of
Geomagnetism and
Aeronomy Scientific
Assembly, Toulouse,
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VARIATION OF AMS AND OF BULK MAGNETIC PROPERTIES IN SEDIMENTARY HOST-ROCKS AS A FUNCTION OF THE DEGREE OF CONTACT METAMORPHISM: CASE STUDY OF THE FOU M ZGUID DYKE (SOUTHERN MOROCCO).

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We investigate the magnetic signature displayed by the sedimentary rocks affected by contact metamorphism around the Foum Zguid dykes. Samples were collected in the host-rocks along cross-sections perpendicular to dykes. Petrographic analysis points out recrystallization and important Fe-metasomatism. The latter process is mainly recorded by the development of widespread, fine-grained hematite disseminations. AMS and bulk magnetic parameters show important variations related to the intensity of contact metamorphism. The latter can affect the composition and/or the distribution of primary magnetic carriers and leads to development of new magnetic phases. Close to Foum Zguid dykes, variation of the bulk magnetic parameters seems related to the observed Fe-metasomatism.

Determination of the magnetic fabric variation during stepwise heating treatments performed in laboratory complemented our study. Magnetic fabric of the samples the less-affected by contact metamorphism becomes similar to that of the most affected ones. Our experiments show that the minimum temperature range required for the beginning of this magnetic fabric transformation is 300 – 400°C, which was then the minimum temperature reached by host-rocks very close to the dyke during intrusion. They indicate that heat alone could be responsible for these measured variations on the magnetic fabric. The evolution of the magnetic fabric close to the dyke clearly results here from thermal effects and not from a particular stress field due to the intrusion.

Magnetic studies prove to be a very sensitive tool to assess the variable intensity of the Fe-metasomatism and recrystallization processes, and the thermal behavior induced by dyke intrusion.

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Assembly, Toulouse,
França, Julho de 2005.*

AMS STUDY OF MESSEJANA (IBERIAN PENINSULA) AND FOUM ZGUID (SOUTHERN MOROCCO) DYKES

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In some segments, the Foux Zguid dyke crops out with 100% of exposure, being thus possible to carry out a detailed structural work and collect full sections of oriented cores for magnetic fabric purposes. The same does not happen with the Messejana dyke because it is usually deeply weathered, which makes it difficult to carry out detailed structural and AMS work in the dyke margins.

In terms of magnetic mineralogy, the two dykes show Ti-poor titanomagnetite as the main magnetic carrier. Preliminary petrographic analysis for the two dykes shows that the main Ti phase is ilmenite, which occurs either as lamellae within spinel (center of the dyke) or as isolated grains (dyke margin). Bulk magnetic properties are similar for the two dykes. However, the possibility of sampling along cross-sections at Foux Zguid dyke allowed the identification of distinct behavior according to distance to the dyke margin. Grain size of the main magnetic carrier decreases towards the center of the dyke, while the natural remanent magnetization and the bulk magnetic susceptibility increase. These characteristics are most probably related with vertical magmatic differentiation.

In the Foux Zguid dyke, only the magnetic susceptibility ellipsoid close to the dyke margin corresponds to that usually found in thin dykes, with the magnetic foliation making a small angle with the dyke margins. Even so, in some sampled sites these first meters display a sharp difference of the interpretable magma flow, which are accompanied by distinct bulk magnetic properties. For Messejana dyke such accuracy of sampling near the margins was not possible to achieve, although it is possible to identify a well defined magnetic fabric. We recently initiate a comparative study in the Foux Zguid region of dykes with thickness varying from meter to hundred meters scale to evaluate flow.

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2005*

MAGNETIC PROPERTIES OF A DOURO MUDDY PATCH CORE (NORTHERN PORTUGUESE CONTINENTAL SHELF)

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2005

To evaluate recent sedimentation characteristics changes, sedimentological and magnetic data of a gravity core with 3.67 m retrieved, were performed at muddy complex (during an IGM mission), located in sandy continental shelf offshore of the Douro River, between 60-130 m depth. Sedimentological analyses allowed to defined three different units for the last 1400 ± 40 BP years (AMS ¹⁴C dating of organic sediment base; Beta analytic Inc.). The lowest unit (3.67 - 3.30 m), it is very well individualised, as it is the coarsest one, with a higher percentage in sand. It is represented by sandy mud and muddy sand layers according to Flemming (2000) classification. It has also the highest values of carbonates and presents the lowest water and organic matter contents. A slightly sandy mud zone intercalated with some few sandy mud and mud layers characterizes the second unit it is comprised between 3.30 – 1.50 m. In general, present the highest mud, water and organic matter contents. The last unit it is the top unit (above 1.50 m) and it is constituted by a slightly sandy mud sequence with a frequent alternation between sandy mud and slightly sandy mud layers. Comparing with the second unit, this unit present a lower mud and organic matter content. Magnetic measurements (magnetic susceptibility (χ), Natural Remanent Magnetization (NRM), Anhysteretic Remanent Magnetization (ARM) and measurement of the hysteresis parameters) reveal too, the presence of these three distinct sedimentation units, with the same limits. In terms of mineral magnetic classes, at the base of the core till a depth of 3.30 m we observe a considerable contribution of the paramagnetic minerals for the magnetic susceptibility signal, around 50%, while for the rest of the core the signal is dominated by ferromagnetic minerals. Isothermal Remanent Magnetization (IRM), (saturation reached for applied fields around 200 mT), S – parameters very close to 1 and hysteresis experiments are in agreement with the presence of the low-coercivity mineral such as magnetite or maghemite. Representative thermomagnetic analyses are characterized by no reversible behaviour and indicate a presence the two magnetic phases, with Curie temperatures around 300°C and 580°C. However, low-temperature analyses no evidences for the presence of magnetite. Then we suggest the maghemite as the main magnetic carrier. ARM measurements display

similar pattern along the core, which indicated similar physics characteristic of the main carrier. The studies of χ reveal an evolution of the concentration of the mineral from the base to the top of the core, where it is possible to observe a significant but regular increase of 3.67 m to 2,70 m. From 2.70 m to the top the values of χ display the same slightly decrease, although, between 2.70 m and 1.50 m, can be observable an oscillation of the values around the mean trend. This limited at 1.50 m is evidenced too when we plot remanent ratio along the core. The inclination of NRM is very stable, around 55° , from the base of the core until a depth of 1.50 m, after what, an irregular pattern is observed.

CONTRASTING MAGMATIC FLOW PATTERNS DURING GRANITE EMPLACEMENT: AN EXAMPLE FROM CENTRAL-NORTHERN PORTUGAL

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 European Geosciences
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Anisotropy of magnetic susceptibility (AMS) has been successfully applied by several researchers to granitic rocks, contributing significantly to the understanding of the emplacement mechanisms of these rocks. In most reported cases, however, this technique was applied to relatively small and circumscribed massifs. Only a few referred to large nested batholiths. The granites of Viseu-Cota and Alcafache, in Central-Northern Portugal, are part of a large composite late-Variscan batholith that crops out in the Central Iberian Zone. Both granites are coarse porphyritic biotitic monzogranites, but the Alcafache granite also contains muscovite. Based on field and petrological data, it has been proposed a close genetic and chronological relationship between the two granites, involving a multiple installation mechanism with partial overlapping in time of consecutive intrusive stages (Azevedo & Nolan, 1998). A full structural characterization by classical methods was not possible, though, due to the low anisotropy of the rocks. In order to overcome these difficulties and improve the understanding of the genesis and emplacement mechanisms of Viseu-Cota and Alcafache granites, an AMS study was carried out, based on 823 oriented cylindrical samples collected from 93 different sites, each site about 1 km from the neighbouring ones. The magnetic susceptibility data were obtained on a Kappabridge-KLY2 instrument (Agico, Brno), working at a fixed frequency of 920 Hz and an applied field of 300 A/m, the anisotropy ellipsoid being estimated from 15 measurements on each sample. The magnetic susceptibility (MS) data show a paramagnetic character for both granites, with average values of 17.3×10^{-5} SI for Viseu-Cota and 12.8×10^{-5} SI for Alcafache granite, which is well correlated with the biotite content of the rock. Taking into account the contribution of paramagnetic phases only, the estimated AMS values are below 3% everywhere within the studied area, except in the vicinity of a local shear zone, where a maximum of 4.6% was reached. The orientations of both magnetic foliation and lineation are clearly different in the two granites and can be summarized as follows: in the Viseu-Cota granite both foliation and lineation are steeply plunging; in contrast, in Alcafache granite the foliation is mostly

moderately to gently dipping and the lineation, with few exceptions, has a consistent NE-SW direction and gentle plunge. Due to the good correlation between the MS ellipsoid and the mineral fabric, as well as the lack of evidence of solid-state deformation, the magnetic fabrics can be equated to the magmatic fabrics. The patterns of magmatic flow inferred from AMS observations suggest that the two magmas have undergone different emplacement kinematics. Given the close genetic and chronological relationship between them, it is proposed that either a rapidly changing tectonics and/or different space conditions during the emplacement processes must have occurred.

USE OF AMBIENT VIBRATION TESTING FOR MODAL EVALUATION OF A 16 FLOOR REINFORCED CONCRETE BUILDING IN LISBON, PORTUGAL.

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This paper presents a description of the experimental and analytical studies performed on a multi-storey office building in the newly residential and office area of Lisbon, Portugal. The building is located in sensitive alluvium soil, near Tagus river – Lisbon. This city was severely damaged by strong magnitude earthquakes e.g. 1531.01.26, 1755.11.01 and 1969.02.28.

The selected building is a 16-storeyed reinforced concrete structure consisting of “oval” shaped flat plate slabs with a central rectangular rigid core. The structure has 12 floors above ground and four basement levels. Ambient Vibration testing was conducted in order to determine natural frequencies, mode shapes and damping ratios. Those parameters were obtained using Artemis software. A FEM model of the structure are presented in this paper and compared.

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Engineering.
Vancouver, B.C.,
Canada, August, 1-6,
2004.

A CASE OF SOIL SLIDING IN THE PATHOLOGY OF A RETAINING STRUCTURE

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ABSTRACT

Sesimbra is a village located on the Portuguese West coastline 70 km South of Lisbon.

It is a site of high cliffs, overlooking the sea, mainly formed by clays. The rainwater that penetrates the soil through permeable layers originates the clays sliding.

Recent construction site in the area started with the execution of a retaining wall with counterforts.

Some time later after a long rainy period the soil sliding created a high earth pressure on the retaining wall that originated the separation between the wall and its counterforts.

The paper describes the pathology and its repair.

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NY Session 5*

UM EXEMPLO SIGNIFICATIVO DE UTILIZAÇÃO DE PAREDES MOLDADAS ANCORADAS - O EURO STADIUM

A SIGNIFICANT EXAMPLE OF DIAPHRAGM WALLS – THE EURO STADIUM

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RESUMO

Refere-se o caso duma parede moldada ancorada, com cerca de 800,0 m de perímetro e altura variando entre os 11,5 m e os 21,5 m, correspondente à contenção periférica do empreendimento Euro Stadium, localizado junto ao Estádio Municipal de Coimbra.

Aborda-se o seu dimensionamento e os principais aspectos construtivos.

ABSTRACT

The Euro Stadium diaphragm walls, with a total length of about 800,0m and with an height varying between 11,5m and 21,5m, located near the Coimbra Stadium, are referred. Design and construction aspects are analysed.

Publicado em:

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de Geotecnia, Aveiro,
2004*

REVESTIMENTOS DE IMPERMEABILIZAÇÃO DE COBERTURAS EM TERRAÇO COM BASE EM MEMBRANAS PREFABRICADAS. COMPORTAMENTO DE JUNTAS DE SOBREPOSIÇÃO

Gonçalves, Manuela

Mestrado em: Construção

Grau Concedido por: IST – Universidade Técnica de Lisboa

Orientadores: Jorge Manuel Grandão Lopes

Provas Concluídas em: 1 de Junho de 2004

A cobertura é o elemento da envolvente exterior do edifício responsável pela vedação superior do espaço habitável. A sua função é complexa e importante porque, relativamente à dos restantes elementos da envolvente os agentes atmosféricos nela actuam mais directa e intensamente.

É o caso da chuva que cai sobre as coberturas geralmente com impacto directo e é susceptível, em especial nas coberturas em terraço, de conduzir a manifestações de humidade nos edifícios. Consequentemente, pode levar à ocorrência de anomalias capazes de impedir a total satisfação das mais elementares exigências de habitabilidade das edificações.

Apesar disso, as coberturas em terraço têm características funcionais e formais que em muitos casos as recomendam ou impõem. No entanto, a constatação frequente do comportamento deficiente deste tipo de cobertura, quase sempre resultante de erros ou descuidos do projecto ou da execução, tem desprestigiado indevidamente o seu uso. Daí reconhecer-se a necessidade de discutir, esclarecer e divulgar as soluções de concepção, constituição e pormenorização construtiva dos sistemas de impermeabilização capazes de conferirem um bom desempenho às coberturas em terraço.

Entre os vários tipos de sistemas de impermeabilização de coberturas em terraço usados em Portugal, começam a ter uma utilização crescente os sistemas fixados mecanicamente de camada única, ou seja, aqueles que na zona corrente da cobertura são formados por uma única membrana, fixa pontual ou linearmente ao suporte por peças apropriadas. Contudo, o desempenho destes sistemas é fortemente condicionado pelo comportamento das ligações entre membranas, isto é, pelo comportamento das suas juntas de sobreposição. Assim, esta dissertação pretendeu contribuir para um melhor conhecimento deste tipo de sistemas de impermeabilização através da avaliação do comportamento das respectivas juntas de sobreposição.

OBRAS SUBTERRÂNEAS: IMPERMEABILIZAÇÃO E DRENAGEM ASSOCIADA

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Mestrado em: Construção

Grau Concedido por: IST – Universidade Técnica de Lisboa

Orientadores: Maria da Graça Alfaro Lopes e Jorge Manuel Lopes de Brito

Provas Concluídas em: 27 de Outubro de 2004

O facto de não existir em Portugal documentação específica sobre a impermeabilização e drenagem associada de obras subterrâneas, gerou a necessária motivação para a selecção deste tema, acrescida ainda pelas inúmeras dificuldades vividas e sentidas pelo autor nos últimos oito anos, enquanto responsável pela realização de diversas obras do género.

Contrariamente ao que seria espectável, as dificuldades mais comuns que surgem na concretização dos trabalhos de impermeabilização têm-se mantido nos últimos anos. Por isso, o presente trabalho tem por objectivo indicar os principais aspectos a ter em consideração no projecto e na execução das diversas actividades inerentes ou interligadas ao sistema de impermeabilização e drenagem associada de obras subterrâneas, de modo a minimizar ou evitar problemas futuros, decorrentes de erros de projecto, de execução e de controlo de qualidade dos materiais e da sua instalação.

É realçada a importância da instalação adequada dos geotêxteis, geomembranas e geocompósitos contemplados nos sistemas de impermeabilização e drenagem associada das obras subterrâneas, de modo a assegurar a durabilidade estimada para as mesmas, sem desvios das condições de operacionalidade para que foram projectadas. São também descritas as tecnologias de instalação adaptadas para os sistemas apresentados e o equipamento disponível para a sua concretização, muito embora as plataformas automáticas não estejam disponíveis entre nós em face do número de obras subterrâneas, da sua tipologia e métodos de trabalho não justificarem o investimento. A metodologia adoptada na elaboração do trabalho assentou em seis fases distintas: recolha de informação técnica sobre a matéria, estudo dos métodos construtivos das estruturas e sua relação com a geologia do terreno; selecção e especificação dos materiais mais adaptados; soluções de impermeabilização e drenagem associada; processos construtivos e suas exigências (metodologia de instalação); controlo de qualidade.



ENGENHARIA DE ELECTRÓNICA DE TELECOMUNICAÇÕES E DE COMPUTADORES

Anuário Científico 2005

ISEL

INTEGRAÇÃO DE EMOÇÃO E RACIOCÍNIO EM AGENTES INTELIGENTES

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Esta dissertação aborda a influência que fenómenos de base emocional podem ter nos processos de raciocínio e tomada de decisão de agentes inteligentes, no sentido de tornar viável a utilização de agentes com esse tipo de capacidades cognitivas, em cenários concretos, onde é exigida uma resposta em tempo-real. São contribuições específicas da tese um modelo de emoção para suporte à modelação de fenómenos emocionais em agentes inteligentes, no qual são enfatizadas as dinâmicas subjacentes ao surgimento desses fenómenos, e um modelo de agente capaz de suportar a modelação da relação entre fenómenos emocionais e cognitivos, tendo por base o carácter dinâmico e contínuo dessa relação. Estes modelos servem de suporte à implementação de mecanismos de regulação e adaptação dos processos de raciocínio e tomada de decisão, capazes de tirar partido da relação entre fenómenos emocionais e cognitivos para focar a actividade cognitiva. Esses mecanismos permitem controlar a utilização dos recursos computacionais envolvidos na actividade cognitiva dos agentes e o tempo disponível para essa actividade cognitiva, bem como tirar partido de experiências passadas para antecipar situações futuras, através da formação de memórias emocionais autobiográficas e da exploração dessas memórias por meio de raciocínio prospectivo. É proposta uma arquitectura de agente genérica, capaz de suportar a implementação de agentes de diferentes tipos e níveis de complexidade, integrando aspectos de base emocional e cognitiva. Como suporte experimental, apresentam-se três protótipos vocacionados para contextos de aplicação distintos: contexto de dinamismo do ambiente variável; contexto com restrições sensoriais e temporais; contexto de raciocínio social.

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Faculdade de Ciências
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Lisboa, 2005.*

DISORDER RELATED OPTICAL PROPERTIES AND ELECTRONIC TRANSPORT IN GALLIUM NITRIDE

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Publicado em:

Dissertação de doutoramento, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Optical properties and electronic transport in gallium nitride (GaN) are studied using a disorder-related approach. Structural characterization by scanning electron microscopy (SEM) and atomic force microscopy (AFM) with GaN samples deposited by a low temperature pulsed laser deposition (PLD) technique reveal nanocrystalline structures with column diameters around 200 nm.

Absorption spectra (transmission/reflection and photocurrent) of n-type GaN show exponential valence band tails with Urbach energies of the order 150-200 meV, which decrease with temperature. Cathodoluminescence (CL) mapping confirms that spatial and energetic fluctuations over a significant range of length and energy scales are present. Photoluminescence (PL) spectra reveal the presence of broad sub gap emission bands centered in the yellow, the blue and the red spectral region. PLD samples show a near band edge (NBE) band as broad as 200 meV.

Transient measurements of photocurrent (TPC), photoluminescence (TPL) and photoreflectance (TPR) all showed clearly non-exponential decays, which most often could be characterized by power law fits. We observed that a variety of effects in TPC and TPL cannot be explained in the framework of the canonical relaxation mechanisms, i.e. the multiple trapping (MT) and the donor acceptor pair (DAP) recombination model.

Consequently, we developed a new analytic model (TR Model) which integrates the complementary experimental evidence of spatial dispersion (DAP recombination) and energetic dispersion (band tails). The model is based on the competition between thermalization and recombination (TR) of excess carriers trapped in states distributed exponentially in energy and localized in space. It describes the PL energy and time dependence in excellent agreement with experiment, and reveals the correlation between TPL and TPC.

All transients can be well described through the thermalization process, i.e. the competition between the total concentrations of free and trapped carriers.

Finally, we apply laser induced grating techniques to characterize minority carrier transport in GaN.

DOES INDEPENDENT COMPONENT ANALYSIS PLAY A ROLE IN UNMIXING HYPERSPECTRAL DATA?

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Independent component analysis (ICA) has recently been proposed as a tool to unmix hyperspectral data. ICA is founded on two assumptions: 1) the observed spectrum vector is a linear mixture of the constituent spectra (endmember spectra) weighted by the correspondent abundance fractions (sources); 2) sources are statistically independent. Independent factor analysis (IFA) extends ICA to linear mixtures of independent sources immersed in noise. Concerning hyperspectral data, the first assumption is valid whenever the multiple scattering among the distinct constituent substances (endmembers) is negligible, and the surface is partitioned according to the fractional abundances. The second assumption, however, is violated, since the sum of abundance fractions associated to each pixel is constant due to physical constraints in the data acquisition process. Thus, sources cannot be statistically independent, this compromising the performance of ICA/IFA algorithms in hyperspectral unmixing. This paper studies the impact of hyperspectral source statistical dependence on ICA and IFA performances. We conclude that the accuracy of these methods tends to improve with the increase of the signature variability, of the number of endmembers, and of the signal-to-noise ratio. In any case, there are always endmembers incorrectly unmixed. We arrive to this conclusion by minimizing the mutual information of simulated and real hyperspectral mixtures. The computation of mutual information is based on fitting mixtures of Gaussians to the observed data. A method to sort ICA and IFA estimates in terms of the likelihood of being correctly unmixed is proposed.

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VELOCITY ESTIMATION OF FAST MOVING TARGETS USING A SINGLE SAR SENSOR

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89, January, 2005*

A new methodology is presented to retrieve slant-range velocity estimates of moving targets inducing Doppler-shifts beyond the Nyquist limit determined by the pulse repetition frequency (PRF). The proposed approach exploits the linear dependence (not subject to PRF limitations) of the Doppler-shift with respect to the slant-range velocity, at each wavelength.

Basically, we propose an algorithm to compute the skew of the two-dimensional spectral signature of a moving target. Distinctive features of this algorithm are its ability to cope with strong range migration and its efficiency from the computational point of view. By combining the developed scheme to retrieve the slant-range velocity with a methodology proposed earlier to estimate the velocity vector magnitude, the full velocity vector is unambiguously retrieved without increasing the mission PRF. The method gives effective results even when the returned echoes of the moving targets and the static ground overlap completely, provided that the moving targets signatures are digitally spotlighted and the signal-to-clutter ratio (SCR) is, roughly, greater than 14 dB. The effectiveness of the method is illustrated with simulated and real data. As an example, slant-range velocities of moving objects with velocities between 6 and 12 times the Nyquist velocity are estimated with accuracy better than 3%.

STRUCTURAL AND COMPOSITION ANALYSIS OF GAN FILMS DEPOSITED BY CYCLIC-PLD AT DIFFERENT SUBSTRATE TEMPERATURES

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GaN films were deposited by cyclic pulsed laser deposition (cyclic-PLD) at different substrate temperatures between 400 and 600 C.°. Alignment of the films along the c-axis, grain size, roughness and conductivity increased with temperature. Surface elemental ratio N/Ga was determined by X-ray photoelectron spectroscopy (XPS) and was smaller for films deposited at higher temperature. A decrease of the resistivity of the films agreed with higher metallic (Ga) surface concentration. Bulk elemental ratio N/Ga, determined by Rutherford backscattering spectroscopy (RBS), was higher than the XPS ratio and showed a very small tendency to decrease with deposition temperature. At 600 C.°, there was evidence of contamination of the films by oxygen probably resulting from diffusion from the sapphire (Al₂O₃) substrate. These results suggest that adjustments in the deposition conditions are needed in order to have high crystal alignment, large grain size and good N/Ga ratio.

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ACTUATORS A 121
(2005) 131-135*

OPTICAL SIGNAL AND IMAGE PROCESSING DEVICE OPTIMIZED FOR OPTICAL READOUT

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Large area ($4 \times 4 \text{ cm}^2$) optical signal and image processing (OSIP) devices were produced at low temperatures by Plasma Enhanced Chemical Vapour Deposition (PE-CVD). The OSIP device consists of two stacked sensing/switching diodes ($p(\text{SiC:H})/i(\text{Si:H})/n(\text{SiC:H})$) with an internal light blocking layer between them and two semitransparent contacts. An optical scanner is used for charge readout. In this work the main emphasis will be put on the analysis of the optical characteristics. The use of a metal grid ($290 \times 290 \mu\text{m}^2$ Cr pixels with $40 \mu\text{m}$ spacing) between the two diodes, working as light screening layer or as floating anode via an a-SiN insulator layer, is analyzed. Its influence on the transfer functions, resolution, responsivity and response time of the sensor is presented. The optical-to-electrical transfer characteristics show high quantum efficiency, broad spectral response, and reciprocity between the optical and the electrical images. When the light screening floating anode is present an effective optical decoupling from both photodiodes is achieved while maintaining a good electrical conductivity and an increased light-to-dark sensitivity. A trade-off is established between sensor design and light pattern and scanner wavelengths in order to minimize the cross talk between the write and the read beams and to improve the light to dark sensitivity. (c) 2004 Elsevier B.V. All rights reserved.

THE MULTI-TEAM FORMATION PRECURSOR OF TEAMWORK

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We formulate the multi-team formation (M-TF) domain independent problem and describe a generic solution for the problem. We illustrate the M-TF preference relation component in the domain of a large scale disaster response simulation environment. The M-TF problem is the precursor of teamwork that explicitly addresses the achievement of several short time period goals, where the work to achieve the complete set of goals overwhelms the working capacity of the team formation space (all teams formed from the finite set of available agents). Decisions regarding team formation are made by the agents considering their own probabilistic beliefs and utility preferences about the whole (known) set of goals to achieve. The RoboCupRescue simulated large scale disaster domain is used to illustrate the design of the preference relation domain specific M-TF component.

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THE MULTI-TEAM FORMATION DEFENSE OF TEAMWORK

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Spanish Association
for Artificial Intelligence,
CAEPIA-05, Pages 259-
268, Universities of
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Santiago de
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de Compostela, Spain,
November 16-18,
2005.*

We formulate the multi-team formation (M-TF) derogation component in the domain of an urban fire disaster. The M-TF problem is the precursor of teamwork that explicitly addresses the achievement of several short time period goals, where the work to achieve the complete set of goals overwhelms the working capacity of the team formation space (all teams formed from the finite set of available agents). Decisions regarding team formation are made considering that team reformation is the means to counteract possible deviations from a desirable teamwork behavioral performance. The RoboCupRescue large scale disaster environment is used to illustrate the design of the derogation domain specific M-TF component.

THE MULTI-TEAM FORMATION DEFENSE OF TEAMWORK

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This paper focuses on agent-to-human presentation of the agent knowledge-level in a multi-agent environment. The presentation skill is regarded as an agent's role - the presenter role, in charge of uncovering what is occurring. In our approach the design of this role is driven by two main concerns: i) the inter-agent knowledge sharing, and ii) the human user monitoring of the knowledge being shared by the agents. In this paper we address these concerns from the agent's ontology commitment perspective. We propose a presenter role model (and its subsequent architecture) centered on the domain and role ontologies. The implementation of the presenter role faces two challenges: one is to cope with diverse knowledge-level representations; the other is to present behavioral knowledge to the human user. In this paper we describe our approach to the implementation challenges and to the materialization of the presenter role model in the context of a multi agent game like experiment. In the experiment, the inter agent communication uses a standard semantic language (FIPA SL) and the agent to user presentation adopts the Java Swing platform independent user interface components. We adopted JADE (FIPA compliant) framework as the basis of the development process. Ontology specifications were built with Protégé ontology editor. We are currently exploring the presenter role monitoring capability in the RoboCupRescue multi-agent environment for simulations in the domain of emergency scenarios of search and rescue behavior within large-scale disasters.

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FORMAÇÃO DE EQUIPAS PARA COMBATE A INCÊNDIO URBANO

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Engenharia de Lisboa
– ISEL, Lisboa,
Portugal, Dezembro
17-18, 2005.*

Neste artigo descreve-se uma abordagem para dimensionar uma equipa de bombeiros para combate a incêndio urbano em ambiente de simulação. A simulação foi realizada no ambiente RoboCupRescue que combina, num mesmo espaço geográfico (e.g. cidade), a evolução de uma catástrofe (e.g. incêndio urbano) e a actuação dos meios (humanos) que visam mitigar os efeitos dessa catástrofe. A abordagem seguida permite determinar o número mínimo de elementos a constituir numa equipa de bombeiros para extinguir um determinado incêndio. Utilizou-se um processo de exploração de conhecimento a partir de um conjunto de treino para construir uma árvore de decisão, recorrendo ao algoritmo de classificação ID3. O conjunto de treino foi obtido a partir da simulação de diferentes situações de incêndio usando o espaço geográfico (mapa) da cidade japonesa de Kobe. São analisados os resultados da avaliação das regras geradas e apresentam-se algumas conclusões sobre os factores que influenciam o critério de formação das equipas.

P-I-N FLEXIBLE IMAGING DEVICES WITH OPTICAL READOUT

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Large area two terminal p-i-n image sensors deposited on plastic substrates were produced at low temperatures (110 degrees C) by PECVD and compared with similar sensors deposited on glass substrates. The same sensing element structure ZnO:Al/p(SiC:H)/i(Si:H)/n(SiC:H)/Al was used in all devices although with different resistivities of the front contact. In this work the efforts are focused mainly on the optimization of the output characteristics of the sensor when fabricated on plastic substrates. The role of the sensor configuration, front contact resistivity and readout parameters on the image acquisition process is analyzed. The optical-to-electrical transfer characteristics show reasonable quantum efficiency under a red light pattern, broad spectral response, and reciprocity between light and image signal. First results show that the sensors deposited on flexible substrate present smaller light to dark sensitivity than those deposited on glass. In both, the non ohmic behavior of the transparent conductive oxide front contact blocks the carrier collection and leads to a surprising linear dependence of the image signal on the applied voltage. (c) 2004 Elsevier B.V. All rights reserved.

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2005

HSDPA CAPACITY ENHANCEMENT USING MIMO IN A PICO-CELL ENVIRONMENT

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The concept of High Speed Downlink Packet Access (HSDPA) has been standardized in 3GPP for UMTS (Universal Mobile Telecommunication System).

The main interest of this paper is the application of MIMO (multiple-input-multiple-output) techniques in order to achieve high data rates in HSDPA. The capacity increase available from deploying MIMO systems is obtained via the potential decorrelation between the channel coefficients of the MIMO radio channel, which can be used to create several parallel sub-channels.

Along with the MIMO technique, it is mandatory to provide a metric of the channel, to be transmitted in the feedback channel by the UE (User Equipment), useful for the Node B (UMTS Base Station) to adapt the downlink transmission rate. The implemented metric is the Shannon spectral efficiency coded using 4 bit per HSDPA frame.

The present paper is organized as follows: Section II introduces the COST 259 Directional Channel Model (DCM) and its integration on the virtual pico-cell deployment area. Section III presents the eigenanalysis and Shannon's spectral efficiency calculation. Section IV presents MIMO simulations applied to HSDPA structure for the standard pico-cell environment using specific scheduling.

The UEs utilization (UE time share over simulation time) standard deviation is introduced as an unfairness measure of the scheduling algorithm.

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International
Conference on
Wireless
Communications and
Applied Computational
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(CD-ROM).*

VERTEX COMPONENT ANALYSIS: A FAST ALGORITHM TO UNMIX HYPERSPECTRAL DATA

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Given a set of mixed spectral (multispectral or hyperspectral) vectors, linear spectral mixture analysis, or linear unmixing, aims at estimating the number of reference substances, also called endmembers, their spectral signatures, and their abundance fractions. This paper presents a new method for unsupervised endmember extraction from hyperspectral data, termed *vertex component analysis* (VCA). The algorithm exploits two facts: 1) the endmembers are the vertices of a simplex and 2) the affine transformation of a simplex is also a simplex. In a series of experiments using simulated and real data, the VCA algorithm competes with state-of-the-art methods, with a computational complexity between one and two orders of magnitude lower than the best available method.

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TUNING THE SPECTRAL DISTRIBUTION OF P-I-N A-SIC : H DEVICES FOR COLOUR DETECTION

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ZnO: Al/p (SiC:H)/i (Si:H)/n (SiC:H) large area image and colour sensor are analysed. Carrier transport and collection efficiency are investigated from dark and illuminated current-voltage (I-V) dependence and spectral response measurements under different optical and electrical bias conditions. Results show that the carrier collection depends on the optical bias and on the applied voltage. By changing the electrical bias around the open circuit voltage it is possible to filter the absorption at a given wavelength and so to tune the spectral sensitivity of the device.

Transport and optical modelling give insight into the internal physical process and explain the bias control of the spectral response and the image and colour sensing properties of the devices. (c) 2004 Elsevier B.V. All rights reserved.

IMAGE AND COLOR SENSITIVE DETECTOR BASED ON DOUBLE P-I-N/P-I-N A-SiC:H PHOTODIODE

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A two terminal image and color sensitive detector based on two stacked sensing/switching p-i-n a-SiC:H diodes is presented. The imaging is performed in a write-read simultaneous process: the write exposure, which converts the optical image into a localized packet of charges and the readout which performs the charge to current conversion by detecting the photocurrent generated by a light beam scanner. By sampling the absorption region at appropriated voltages it is possible to extract separately the RGB integrated information with a good rejection ratio. Readout of 1000 lines per second is achieved allowing continuous and fast color recognition and image detection. A trade-off between the sensing and the switching diodes thicknesses is established in order to enhance the green recognition. When it is used a thin a-SiC:H, optimized for red transmittance and blue collection, and a switching absorber thick enough to absorb most of the incoming green light, the detector behaves itself as a filter giving information about the wavelength and the position of the optical image. © 2005 Materials Research Society.

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YBRID CODE DELAY ESTIMATOR FOR GPS/GALILEO BOC SIGNALS USING THE INNOVATIONS APPROACH

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6-8, 2005, Tomar,
Portugal.*

Binary offset carrier (BOC) modulation was adopted for modernized military GPS and is also considered for the European Navigation System Galileo. Although it performs better than the conventional BPSK modulation, the BOC waveforms have autocorrelation functions with multiple peaks that lead to potential tracking ambiguities. To mitigate this problem we consider an architecture where the conventional structure (phase-lock loop and delay-lock loop) is replaced with a bank of stochastic nonlinear filters that estimate the incoming carrier phase, frequency and frequency-rate (modeled as the components of a state vector). The code discriminator is a weighted sum of code delays with the weights being nonlinear functions of the filters innovations. A look-up table allows to convert the discriminator output into a code delay estimate. The proposed receiver is an open-loop structure in terms of the phase/frequency and is an hybrid (open/closed) structure in terms of the code loop.

TRAFFIC ANALYSIS AT THE RADIO INTERFACE IN UMTS FDD

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The performance of a UMTS network depends on the diversity of services and applications, which have different requirements in terms of network resources and quality of service. In this paper, the study of a single UMTS cell obtained via a simulation tool, considering a diversity of services, different service penetration and distinct resources needs is presented. This study includes network link budget calculation, propagation model estimation and interference analysis. Eight service types are implemented: Speech, Video Telephony, Streaming Multimedia, Web Browsing, Location Based Services, MMS, Email and File Download. A statistical approach is taken for the traffic source models, the call/session generation and the duration process for each service. For traffic analysis purposes, three implementation scenarios, have been considered, Business, SOHO and Mass-Market, corresponding to a different service characterisation and utilisation. It is observed that, depending on the service combination, the population density admitted in the system can vary between 300 and 10 000 pop/km², for the scenarios considered.

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Telecommunications,
Tomar, Portugal,
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([http://www.lx.it.pt/con
ftele2005/](http://www.lx.it.pt/con
ftele2005/))*

SOFT-SWITCHING DC-DC CONVERTERS FOR CMOS INTEGRATION

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This paper presents a first study of resonant converter topologies targeted for CMOS integration. A new method to design very-high frequency (MHz) switching Quasi-Square-Wave converters targeted for CMOS implementation is presented. Simulation work based on a $0,35\mu\text{m}$ CMOS process device modelling revealed distinct problems for this soft-switched topology, when compared to the discrete implementation. A ZVS QSW buck converter was designed for a switching frequency in the range of hundreds of MHz. Future work directions are pointed out according to the identified problems.

SPECTRAL SENSITIVITY AND COLOR SELECTIVITY IN MULTILAYER STACKED DEVICES

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In this work, an attempt of full color discrimination is presented using as sensitive devices multilayer stacked structures (p(SiC:H)/i(SiC:H)/n(SiC:H) /p(SiC:H)/i(Si:H)/n(Si:H)) sandwiched between two transparent conductive contacts. The thickness and the absorption coefficient of the front p-i-n cell is optimized for blue collection and red transmittance and the thickness of the back one adjusted to achieve full absorption in the green and high collection in the red spectral ranges. The current-voltage characteristics and the spectral sensitivity under different electric and optical bias conditions and light fluxes are analyzed. Results show that color selectivity is achieved by tuning the spectral sensitivity at different applied voltages. A physical model supports the results.

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IMPROVING HSDPA PERFORMANCE USING MIMO IN A UMTS MACRO-CELL NETWORK

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The aspects of applying MIMO techniques to the UMTS HSDPA transmission, in order to increase transmission rate in UTRAN are introduced. It is shown that Shannon capacity measure, working as the uplink transmitted channel metric, performs a major role on transmission rate determination, Frame Error Rate estimation, and scheduling at the Node B. A UMTS HSDPA simulator using MIMO techniques was developed. It allowed to estimate the MIMO capacity enhancement to the UMTS HSDPA system and to conclude that overall MIMO usage increases UMTS HSDPA system performance.

FINE-TUNING OF THE SPECTRAL COLLECTION EFFICIENCY IN A MULTILAYER JUNCTION THROUGH THE LSP TECHNIQUE

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We report in this paper the recent advances we obtained in optimizing a color image sensor based on the LSP technique. A device structure based on a a-SiC:H/ a-Si:H pin/pin tandem structure has been tested for a proper color separation process that takes advantage on the different filtering properties due to the different light penetration depth at different wavelengths inside the a-Si:H and a-SiC:H absorbers. Under reverse bias the green and the red images give, in comparison with previous tested structures, a weak response, while this structure shows a very good recognition of blue color, leaving a good margin for future device optimization in order to achieve a complete and satisfactory RGB image mapping. The physics behind the device functioning is explained by recurring to a numerical simulation of the internal electrical configuration of the device in dark and under different wavelength irradiations. Considerations about conduction band offsets, electrical field profiles and inversion layers will be taken into account to explain the optical and voltage bias dependence of collected photocurrent.

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MAXIMIZING THROUGHPUT USING HSDPA WITH MIMO IN UMTS MACRO-CELL ENVIRONMENT

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Spring 2005,
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8888-7 (CD-ROM).*

The aspects of applying MIMO techniques to the UMTS HSDPA transmission, in order to increase transmission rate in UTRAN are introduced. It is shown that Shannon capacity measure, working as the uplink transmitted channel metric, performs a major role on transmission rate determination, Frame Error Rate estimation, and scheduling at the Node B. A UMTS HSDPA simulator using MIMO techniques was developed. It allowed to estimate the MIMO capacity enhancement to the UMTS HSDPA system and to conclude that overall MIMO usage increases UMTS HSDPA system performance.

DIRICHLET SOURCES APPLIED TO HYPERSPPECTRAL UNMIXING

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Linear unmixing decomposes a hyperspectral image into a collection of reflectance spectra, called endmember signatures, and a set of abundance fractions vectors (one vector per pixel). This paper introduces a new method to unmix hyperspectral data, where abundance fractions are modelled as Dirichlet sources. This model forces abundance fractions to be non-negative and to have constant sum on each pixel. The mixing matrix is inferred by an expectation-maximization (EM) type algorithm. The performance of the method is illustrated using simulated and real data.

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PARTIAL CORRELATION TECHNIQUE FOR THE ACQUISITION OF WEAK GPS/GALILEO SIGNALS

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Cambridge, MA, USA.*

Modernized civil GPS and the Galileo system utilize twochannel navigation signals: a data channel, carrying navigation data, and a dataless pilot channel. This work addresses the problem of cold acquisition of weak twochannel navigation signals in a software receiver. We propose an algorithm to compute partial correlations between the incoming signal and the locally-generated code which allows the simultaneous search of all primary code phases in a Doppler bin. Using circular correlation this technique is also able to deal with the secondary code transitions. Since the algorithm is based on FFTs it is very efficient from the computational point of view. Different approaches, with and without channels combination, and with coherent and non-coherent combination of primary code integrations, are analyzed, simulated and compared with alternative solutions.

IMPROVING MULTIPATH MITIGATION IN GPS/GALILEO BOC SIGNALS WITH GATING FUNCTIONS

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A new multipath mitigation technique is proposed for binary offset carrier (BOC) signals using the concept of gating function originally conceived for GPS C/A. Instead of correlating the incoming signal with early and late versions of the locally-generated BOC signal, as in the conventional narrow correlator receiver, we use specially-tailored pulses that diminish the number of potential false-lock points of the code discriminator and enhance the robustness to multipath. The multipath mitigation capability of the proposed receiver is analyzed and compared with the narrow correlator and the double-delta (HRC) solutions. Results obtained with BOC(n,n) and BOC(2n,n) signals (both types foreseen for the modernized GPS and the European GNSS, Galileo) show that this method efficiently eliminates the ranging errors due to multipath in the medium and long delay regions, thus comparing favorably with the conventional receiver correlation techniques.

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61.st Institute of
Navigation Annual
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RELEVANCE FEEDBACK IN CBIR USING THE RLS CLASSIFIER

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The Relevance Feedback has been used to improve the performance of CBIR algorithms. This paper presents a relevance feedback method based on the regularized least squares classifier, and a technique to select feedback information in order to increase the learning rate. Experimental results are presented in the paper to illustrate the performance of the proposed relevance feedback method.

Publicado em:

*EURASIP Conference
on Speech and Image
Processing, Multimedia
Communications and
Services, Smolenice,
June 2005.*

ITSIBUS – JINI AND RADIO IDENTIFICATION TECHNOLOGIES UNDERLYING INTEROPERABILITY THROUGH A REAL LIFE OPEN SERVICE ORIENTED TOLL, MANAGEMENT SYSTEM FOR THE PAN-EUROPEAN MOTORWAY NETWORK

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The ITSIBUS (Intelligent Transport Systems Interoperability Bus) architecture was developed in Portugal in a joint research project involving ISEL (an academic and research Institute), BRISA (the biggest motorway management company in Portugal) and WhatEverSoft (the first Sun Authorized Java Center in Portugal). It aimed to develop an open, service oriented architecture for a toll management system in order to promote interoperability among systems from different vendors and to the Pan-European motorways network. The ISIBUS architecture is a peer-to-peer service architecture where discovery and advertisement mechanisms and event registration and subscription are used to establish a community of peer services running on systems (execution containers). These services present standard interfaces and implement toll specialized functionalities like car identification, car classification, and license plate recognition from others. The services run on systems that beyond the functional services, implement specialized system services (core services) like administration, configuration and security. The ISIBUS was primarily motivated by the need for a “plug-and-work” infrastructure where systems from different vendors can be integrated in an open toll management system. Another challenge was established by the need to construct a Pan- European motorway toll infrastructure where cars can use the same payment facilities across all European countries. This talk presents and discusses a real life implementation of the ITSIBUS architecture using JINI and DSRC/RFID technology.

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Moscone,
San Francisco
Session BOF (Birds-of-
a-Feather) – 904.*

SIMULTANEOUS USE IN MOBILE COMMUNICATIONS

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Vehicular Technology
Conference,
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(<http://www.vtc2005spring.org/>)*

Integration, inter-working and convergence of wireless systems are becoming a closer reality. These lead to the possibility of an end user to employ simultaneously several services through different systems and operators with a multi-service, multi-system and multi-operator mobile terminal. In the present paper a coherent set of concepts of simultaneous use is identified, generated by a space of simultaneous use where services, systems and operators act as building components. A high level analysis is performed, where several pros and cons are identified. Several parameters are listed for the evaluation of simultaneous use concepts (e.g., cost, throughput and complexity), depending on taking a users' or an operators' perspective. One of the largest benefits of this systematic identification of simultaneous use concepts is the identification, from the perspective of users and operators, of essential R&D issues on inter-working and integration, which will lead to a promising pervasive wireless communications future.

VIRTUAL TOLLING SYSTEM

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Direct payment of motorway toll on expressways and motorways is nowadays a common situation. Toll payment besides finance construction of new roads and their consequent maintenance, it is also a good mechanism to control and manage traffic on motorways. The current manual and electronic tolling infrastructure generates road pollution and exploration additional costs. This paper propose a system which avoids tolling structures, a so called Virtual Tolling System (VTS). To enable monitor mobility on motorways the Global Positioning System (GPS) was used as a vehicle positioning sensor. In order to have tolling payment messages among others the Global System for Mobile Communications (GSM) is used. This paper propose a complete solution where the VTS system algorithms, databases formats and prototype are described. The VTS provides great functionality and may be integrated in future electronic payment systems offering extended transportation services for customers.

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Radioengineering
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Czech Republic,
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(<http://wes.feec.vutbr.cz/urel/radioeng/>)*

VIRTUAL TOLL GATE SYSTEM

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May 2005
(<http://wes.feec.vutbr.cz/urel/radioeng/>)*

The mobile communications systems are, nowadays, very common in the user's everyday life. On the other hand, applications based on the satellite location system are experiencing a strong growth among navigation systems applied to the motor car industry. The contents of this paper is to present a Virtual Toll Gate System, developed in partnership with a colleague, during the final project to get the degree on Systems of Telecommunications and Electronics Engineering in the Higher Institute on Engineering of Lisbon (ISEL). This project aims to effect the toll gate payment without the need of physical infrastructure construction. The Virtual Toll Gate System is composed for a device that must be installed in the mobile vehicles, to communicate with the Toll Gate Management Centre (TGMC). The toll gates are substituted by geographic coordinates, provided by Global Positioning System (GPS), together with services offered by Global System for Mobile Communications (GSM). This system promotes the interoperability of the charging Toll Gate Systems at an European level. Two prototypes were developed to test the algorithms of the Virtual Toll Gate System; it was also built an application that handles payment messages received from the remote devices for a later delivery to a Toll Gate Management Centre (TGMC). The messages are sent using GSM services, passing through the Internet or by a Short Message Service (SMS).

SIGNAL SUBSPACE IDENTIFICATION IN HYPERSPPECTRAL LINEAR MIXTURES

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Hyperspectral applications in remote sensing are often focused on determining the so-called spectral signatures, i.e., the reflectances of materials present in the scene (endmembers) and the corresponding abundance fractions at each pixel in a spatial area of interest. The determination of the number of endmembers in a scene without any prior knowledge is crucial to the success of hyperspectral image analysis. This paper proposes a new mean squared error approach to determine the signal subspace in hyperspectral imagery. The method first estimates the signal and noise correlations matrices, then it selects the subset of eigenvalues that best represents the signal subspace in the least square sense.

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Pattern Recognition and Image Analysis, Jorge S. Marques, Nicolás Pérez de la Blanca and Pedro Pina editions, *Lecture Notes in Computer Science series*, Springer-Verlag, Vol. 3523, Nº 2, pages 207-214, IbPRIA, June 2005.

REMOTE TRAIN DETECTION SYSTEM

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International Congress
on Sound and
Vibration, Lisbon,
Portugal, July 2005*

Nowadays, there are already tested methods for local detection of present or passing trains. However, the presented work is based upon an idea of developing a system that performs remote train detection and an estimation of the distance to the train. The detection method is inspired on the operation of the sonar, which contains a transmitter and a receiver. The transmitter generates acoustic pulses, whereas the receiver deals with the received echoes, which will be post-processed, applying two proposed techniques. The rail can be seen as a system characterized by a specific transfer function. Hence, having knowledge of the rail frequency response and of its acoustic behaviour, an appropriate transmitting frequency is chosen for the pulses as well as their repeating interval. Two techniques to estimate the distance from the transmitter to the train are suggested: the cross-correlation method and the lock-in amplifier method. Simulations with real signals are made for testing the efficiency of the proposed methods, as well as the robustness to the noise. In the full paper, field experiments performed in real situations will be presented. Two approaches are attempted: 1) having the received echo in the same rail where the transmitter circuit is coupled to, or 2) having that echo on the other rail, assuming that the train will pass the pulse from one rail to the other through the wheels. Due to practical groundwork constraints, such as the acoustic signal decay along the rail and high acoustic conductivity through the sleepers, the above proposed methods were not as successful as they were in the simulations. In order to overcome these problems, a new method is suggested for the remote detection of the train, based on the rail vibrations spectral analysis when the rail is being excited by a moving train.

A-SiC:H/A-Si:H TANDEM STRUCTURE ANALYSIS FOR RGB COLOR RECOGNITION IN LSP DEVICES

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A device structure based on a a-SiC:H/a-Si:H pin/pin tandem structure is proposed for a proper color separation process that takes advantage of the different light spectrum filtering properties of the a-Si:H and a-SiC:H absorbers. We have analyzed a tandem pin–pin device with the following structure deposited using the plasma enhanced chemical vapor deposition (PECVD) technique: ITO/p-type a-SiC:H (20 nm)/a-SiC:H (200 nm)/n-type a-SiC:H (20 nm)/p-type a-SiC:H (20 nm)/a-Si:H (1500 nm)/n-type a-Si:H (50 nm)/ITO. Carbon concentration in the top a-SiC:H cell produces an optical gap of about 2.0 eV. A numerical simulation of the internal electrical configuration of the device under different wavelength radiation supports our analysis of the device operation. The bias dependence of the device output is explained by taking into account, from the point of view of the color sensor applications, considerations about an asymmetric reaction of the internal electric fields to the externally imposed forward bias and a self-biasing effect of the sub-cells under certain unbalanced light generation of carriers. The simulation shows that this structure permits a good recognition of blue color under reverse bias and red color under forward bias conditions. The acquisition of a satisfactory RGB image mapping by controlling the applied bias is possible but remains problematic due to the poor separation of the green component at any value of the applied bias. A simple algorithm is proposed to deduce the green component of the light by combining the previously acquired information about the total intensity of the incident radiation and about the blue and red components.

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September 2005,
Journal of Non-
Crystalline Solids, in
Press.*

LOW LEAKAGE CURRENT A-Si:H/A-SiC:H N-I-P PHOTODIODE WITH CR/A-SiN_x FRONT CONTACT

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Crystalline Solids, in
Press.

This paper presents the design and fabrication process of an a-Si:H/a-SiC:H heterojunction n-i-p photodiode developed for low-level light detection applications. The critical fabrication issues associated with deposition of device-quality materials, tailoring of defects at the i-p interface, film patterning, junction passivation, and contact formation are discussed. A significant reduction of the leakage current down to ~ 10 pA/cm² at reverse bias of 1 V has been achieved by the introduction of ~ 2 nm graded and ~ 4 nm a-SiC:H buffer layers between the i- and p-layers. To preserve interface integrity, a semi-transparent Cr film with a-SiN_x anti-reflection coating is used as a front contact. It is found that such contact induces lower leakage than transparent conductive oxide (TCO) contacts, which can cause a degradation of the p-i interface. A drawback of the semi-transparent metal contact is the optical loss, which can be minimized by thinning the metal layer and optimizing the anti-reflection coating. Quantum efficiency up to 52% is achieved for the optimized photodiode.

THE LASER SCANNED PHOTODIODE: THEORETICAL AND ELECTRICAL MODELS OF THE IMAGE SENSOR

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The laser scanned photodiode (LSP) presents a new concept of image sensor with application in fields where low cost, large area and design simplicity are of major importance. Over the past few years this type of sensor has been under investigation and development, where several structures have been tested and characterized. In this work we present the physical explanation of device operating principle, with recourse to numerical simulation applied to structures with different compositions of the doped layers. An electrical model for this type of device is presented, enabling a fast evaluation of the device characteristics by means of an electrical simulation program.

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Crystalline Solids, in
Press.*

TRACKING WITH BAYESIAN NETWORKS: EXTENSION TO ARBITRARY TOPOLOGIES

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Conference on Image
Processing (ICIP05),
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Sept. 2005, Page(s):11
- 402-5*

It was recently proposed an object tracking method which is able to deal with object occlusions and group tracking, using Bayesian networks. The Bayesian network (BN) tracker has shown promising results in difficult situations but its architecture is limited to a maximum of 2 parents/2 children per node, in order to avoid the combinatorial explosion and difficult network generation procedures from the video signal. This paper addresses the major limitation of the BN tracker and presents a method to generalize the tracker to cope with arbitrary topologies, allowing the tracker to operate in more complex scenes.

LIGHT FILTERING IN A-SiC:H MULTILAYERS STACKED DEVICES USING THE LSP TECHNIQUE

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Light filtering in a-SiC:H stacked multilayer devices is analyzed, using the Laser Scanned Photodiode technique. Results show that the p-i-n-p-i-n device, under appropriated read-out voltages, behaves itself as an imager and a filter giving information not only on the position where the optical image is absorbed but also on its wavelength and intensity. Identification of the red, green and blue components of the spectrum and simultaneous image recognition were achieved at read-out voltages that are able to cancel the self-bias effect due to the different light penetration depth. These voltages shift from positive to negative values as the wavelength of the impinging photons across the back absorber increases. A numerical simulation supports the color filter analysis.

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Journal of Non-
Crystalline Solids, in
Press.*

SPICE MODEL FOR A LASER SCANNED PHOTODIODE TRICOLOR IMAGE SENSOR

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Crystalline Solids, in
Press.*

A SPICE model of the three color a-SiC:H/a-Si:H p-i-n/p-i-n detector operation is presented. The equivalent electric circuit able to describe the behavior of the multilayer structure under non-uniform illumination is composed of two series connected diodes, representing the p-i-n structures, with two non-linear current sources in parallel, representing the photogeneration for different steady-state RGB illumination, with their values depending on the light penetration depth and intensity of the impinging light. This device represents the 1D model of the Laser Scanned Photodiode and may be interconnected in a 2D array through resistors, modeling the high resistivity of the a-SiC:H layers. Electrical simulations were performed for different illumination conditions, and they are compared with the experimental data. The influence of the electrical model parameters on sensor characteristics is analyzed. A physical model supported by the electrical simulation gives insight into the methodology used for image representation and color discrimination.

RADIATION-INDUCED DEFECTS IN A-SI:H BY 1.5 MEV HE₄ PARTICLES STUDIED BY PHOTOCONDUCTIVITY AND PHOTOTHERMAL DEFLECTION SPECTROSCOPY

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We report radiation effects on intrinsic a-Si:H thin films subjected to a 1.5 MeV He⁴ beam for particle fluences up to 10¹⁶ cm⁻². Photothermal deflection spectroscopy is used to obtain information on the sub-gap density of states. Photoconductivity detects changes in the $\mu\tau$ -product of the electrons. Steady-state photocarrier grating technique is used for measuring the ambipolar diffusion length and estimating the hole $\mu\tau$ -product. The 1.5 MeV He⁴ beam radiation results in pronounced changes in the a-Si:H absorption spectrum. Optical absorption due to deep defects increases with particle fluence by more than one order of magnitude. Electronic transport properties consistently degrade with increasing particle fluence and correlate with the density of radiation-induced defects.

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Crystalline Solids, in
Press.*

OPEN MULTI-TECHNOLOGY SERVICE ORIENTED ARCHITECTURE FOR “ITS” BUSINESS MODELS: THE ITSIBUS ETOLL SERVICES

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 Editors: Luis M. Camarinha-Matos, Hamideh Afsarmanesh, Angel Ortiz. ISBN: 0-387-28259-9 Chapter: pp. 439 - 446

AbstractThe development of integrated solutions made of systems based on different technologies, adopting different implementation approaches and different versions is a complex challenge. The lack of standards or differences in implementations when they exist, are important obstacles to the construction of integrated, flexible and agile solutions. The incorporation of systems from different vendors and systems that evolve to answer innovation processes, suggests the advantage for a multi-technology systems strategy. This paper discusses the ITSIBus approach based on, a multi-technology service oriented infrastructure where specialized pluggable systems run services following a peer to peer architecture. The multi-technology approach is based on the discussed System Broker concept. The agility required by a crescent number of collaborative business process requires an advanced flexibility from the ICT technological infrastructure. The ITSIBus approach is also discussed as a grounding platform to support enterprise collaborative networks considering that services in different companies are based on different technologies.

A NEW REALISTIC VEHICULAR MOBILITY MODEL FOR WIRELESS NETWORKS

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In this paper a novel realistic vehicular mobility model is introduced. It captures the moving-in-groups, conscious traveling, and introduces the concept of smart traveling while following drivers' social behavior extracted from inquiries and experimental traffic measurements. Under the model, a routing algorithm is considered. The routing algorithm minimizes the distance to a target on a step by step form, in every street crossing. This is done under a hierarchic street level structure that optimizes travel speed and quality. The mobility model was simulated for Lisbon case study and directional statistical results were compared with experimental measurements from Lisbon Municipality control center. The output shows a good correlation between simulated and experimental values.

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8th International Symposium of Wireless Personal Multimedia Communications 2005, Aalborg, Dinamarca, 18-22 de Setembro de 2005, (ISI), pp 1805-1809.

A TWO TERMINAL OPTICAL SIGNAL AND IMAGE PROCESSING P-I-N/P-I-N IMAGE AND COLOUR SENSOR

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A two terminal optically addressed image processing device based on two stacked sensing/switching p-i-n a-SiC:H diodes is presented. The charge packets are injected optically into the p-i-n sensing photodiode and confined at the illuminated regions changing locally the electrical field profile across the p-i-n switching diode. A red scanner is used for charge readout. The various design parameters and addressing architecture trade-offs are discussed. The influence on the transfer functions of an a-SiC:H sensing absorber optimized for red transmittance and blue collection or of a floating anode in between is analysed. Results show that the thin a-SiC:H sensing absorber confines the readout to the switching diode and filters the light allowing full colour detection at two appropriated voltages. When the floating anode is used the spectral response broadens, allowing B&W image recognition with improved light-to-dark sensitivity. A physical model supports the image and colour recognition process.

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Sensors and Actuators A: Physical, Volumes 123-124, 23 September 2005, Pages 331-336 Eurosensors XVIII 2004 - The 18th European conference on Solid-State Transducers

MOTION COMPENSATED REFINEMENT FOR LOW COMPLEXITY PIXEL BASED DISTRIBUTED VIDEO CODING

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Distributed video coding (DVC) is a new coding paradigm that enables to exploit video statistics, partially or totally at the decoder. A particular case of DVC, Wyner-Ziv coding, deals with lossy source coding with side information at the decoder and allows a shift of complexity from the encoder to the decoder, theoretically without any penalty in the coding efficiency. The Wyner-Ziv solution here described encodes each video frame independently (intraframe coding), but decodes the same frame conditionally (interframe decoding). At the decoder, motion estimation and compensation tools are responsible to obtain an accurate interpolation of the original frame using previously decoded (temporally adjacent) frames. This paper proposes a novel approach to improve the performance of pixel domain Wyner-Ziv video coding by using a motion compensated refinement of the decoded frame and use it as improved side information. More precisely, upon partial decoding of each frame, the decoder refines its motion trajectories in order to achieve a better reconstruction of the decoded frame.

Publicado em:

IEEE International Conference on Advanced Video and Signal Based Surveillance, Como, Italy, September 2005.

IMPROVING FRAME INTERPOLATION WITH SPATIAL MOTION SMOOTHING FOR PIXEL DOMAIN DISTRIBUTED VIDEO CODING

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and Image Processing,
Multimedia
Communications and
Services, Slovak
Republic, July 2005.*

Distributed video coding (DVC) is a new compression paradigm based on two key Information Theory results: the Slepian-Wolf and Wyner-Ziv theorems. A particular case of DVC deals with lossy source coding with side information at the decoder (Wyner-Ziv) and enables to shift the coding complexity from the encoder to the decoder. The solution here described is based on a very lightweight encoder leaving for the decoder the time consuming motion estimation/compensation task. In this paper, the performance of the pixel domain distributed video codec is improved by using better side information derived by motion compensated frame interpolation algorithms at the decoder. Besides forward and bidirectional motion estimation, a spatial motion smoothing algorithm to eliminate motion outliers is proposed. This allows significant improvements in the rate-distortion (RD) performance without sacrificing the encoder complexity.

SIDE INFORMATION EXTRAPOLATION FOR LOW-DELAY PIXEL-DOMAIN DISTRIBUTED VIDEO CODING

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Distributed Video Coding (DVC) is a new video coding approach based on the Wyner-Ziv theorem. Unlike most of the existing video codecs, each frame is encoded separately (either as a key-frame or a Wyner-Ziv frame) which results in a simpler and lighter encoder since complex operations like motion estimation are not performed. The previously decoded frames are used at the decoder to estimate the Wyner-Ziv frames – the frames are coded independently but jointly decoded. To have a low-delay codec, the side information frames (estimation of the Wyner-Ziv frames to be decoded) must be extrapolated from past frames. This paper proposes a robust extrapolation module to generate the side information based on motion field smoothening to provide improved performance in the context of a low-delay pixel-domain DVC codec.

Publicado em:

International Workshop on Very Low Bitrate Video, Sardinia, Italy, September 2005.

IMPROVED CORRELATION NOISE STATISTICS MODELING IN FRAME-BASED PIXEL DOMAIN WYNER-ZIV VIDEO CODING

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Distributed source coding principles have been recently applied to video coding in order to achieve a flexible distribution of the complexity burden between the encoder and the decoder. In this paper we elaborate on a pixel based Wyner-Ziv video codec that shifts all the complexity of the motion estimation phase to the decoder, thus achieving light encoding. In the literature, the statistics of correlation noise between the frame to be encoded and the motion-compensated side information available at the decoder is modeled as a Laplacian distribution. In this paper we elaborate on this topic and we show that a better model can be fitted, achieving a substantial coding efficiency gain. Moreover we discuss the effect of using a side information computed either from perfectly reconstructed (lossless) or from quantized neighboring frames.

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A COLLABORATIVE NETWORK CASE STUDY: THE EXTENDED “VIAVERDE” TOLL PAYMENT SYSTEM

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The extended Via-Verde business model is presented and discussed as a case study of an enterprise collaborative network. In order to offer Via-Verde clients the possibility to use the installed RFID transponder to automatically pay services in car parking areas and gas stations, a complex collaborative enterprise network comprising a diversity of business models, was established. Besides banks and clearing, there are other players involved. The car parking area owners, co-located shops, and companies offering employees parking facilities are examples of such players. The life cycle management of the underlying distributed business process requires a new framework able to deal with the distribution of contributing actors and the need to guarantee interoperability among the panoply of heterogeneous systems. The paper focuses on the requirements for a technological platform to deal with such complex enterprise network. A service oriented infrastructure developed for toll management systems is taken as the baseline for supporting the new enterprise collaborative processes.

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ESTIMATION OF SIGNAL SUBSPACE ON HYPERSPECTRAL DATA

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Dimensionality reduction plays a crucial role in many hyperspectral data processing and analysis algorithms. This paper proposes a new mean squared error based approach to determine the signal subspace in hyperspectral imagery. The method first estimates the signal and noise correlations matrices, then it selects the subset of eigenvalues that best represents the signal subspace in the least square sense. The effectiveness of the proposed method is illustrated using simulated and real hyperspectral images.

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Image and Signal Processing for Remote Sensing XI, Lorenzo Bruzzone editions, Proceedings of SPIE Vol. 5982 pages 191-198, September 2005.

IMAGE AND COLOR RECOGNITION USING AMORPHOUS SILICON P-I-N PHOTODIODES

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Large area hydrogenated amorphous silicon single and stacked p-i-n structures with low conductivity doped layers are proposed as monochrome and color image sensors. The layers of the structures are based on amorphous silicon alloys (a-Si_xC_{1-x}:H). The current-voltage characteristics and the spectral sensitivity under different bias conditions are analyzed. The output characteristics are evaluated under different read-out voltages and scanner wavelengths. To extract information on image shape, intensity and color, a modulated light beam scans the sensor active area at three appropriate bias voltages and the photoresponse in each scanning position ("sub-pixel") is recorded. The investigation of the sensor output under different scanner wavelengths and varying electrical bias reveals that the response can be tuned, thus enabling color separation. The operation of the sensor is exemplified and supported by a numerical simulation.

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A TWO TERMINAL OPTICAL SIGNAL AND IMAGE PROCESSING P-I-N/P-I-N IMAGE AND COLOUR SENSOR

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A two terminal optically addressed image processing device based on two stacked sensing/switching p-i-n a-SiC:H diodes is presented. The charge packets are injected optically into the p-i-n sensing photodiode and confined at the illuminated regions changing locally the electrical field profile across the p-i-n switching diode. A red scanner is used for charge readout. The various design parameters and addressing architecture trade-offs are discussed. The influence on the transfer functions of an a-SiC:H sensing absorber optimized for red transmittance and blue collection or of a floating anode in between is analysed. Results show that the thin a-SiC:H sensing absorber confines the readout to the switching diode and filters the light allowing full colour detection at two appropriated voltages. When the floating anode is used the spectral response broadens, allowing B&W image recognition with improved light-to-dark sensitivity. A physical model supports the image and colour recognition process.

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ENHANCED SHORT WAVELENGTH RESPONSE IN LASER-SCANNED-PHOTODIODE IMAGE SENSOR USING AN A-SiC : H/A-Si : H TANDEM STRUCTURE

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We report in this paper the recent advances we obtained in optimizing a color image sensor based on the laser-scanned-photodiode (LSP) technique. A novel device structure based on a a-SiC:H/a-Si:H pin/pin tandem structure has been tested for a proper color separation process that takes advantage on the different filtering properties due to the different light penetration depth at different wavelengths a-SM and a-SiC:H. While the green and the red images give, in comparison with previous tested structures, a weak response, this structure shows a very good recognition of blue color under reverse bias, leaving a good margin for future device optimization in order to achieve a complete and satisfactory RGB image mapping. Experimental results about the spectral collection efficiency are presented and discussed from the point of view of the color sensor applications. The physics behind the device functioning is explained by recurring to a numerical simulation of the internal electrical configuration of the device.

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EMBEDDING A BLOCK-BASED INTRA MODE IN FRAME-BASED PIXEL DOMAIN WYNER-ZIV VIDEO CODING

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Distributed source coding principles have been recently applied to video coding in order to achieve a flexible distribution of the complexity burden between the encoder and the decoder. In this paper we elaborate on a pixel based Wyner-Ziv video codec that shifts all the complexity of the motion estimation phase to the decoder, thus achieving light encoding. We observe that the correlation noise statistics describing the relationship between the frame to be encoded and the side information available at the decoder is not spatially stationary. For this reason we introduce a mode decision scheme either at the encoder or at the decoder in such a way that when the estimated correlation is weak we opt for intra coding on a block-by-block basis. Moreover we discuss the effect of using a side information computed either from lossless or from quantized frames.

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A 28.5GHZ MONOLITHIC CASCODE LNA WITH 70GHZ FT SIGE HBTS

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This paper presents the design and experimental results of a monolithic cascode LNA for 28.5GHz applications using SiGe HBTs. It shows that designing circuits at frequencies beyond $f_T/3$ is possible. The best experimental results are obtained at 26GHz with a 3.3V supply voltage: $|S_{21}| = 10.4\text{dB}$, input and output matching better than -10dB . The measured noise figure is 6.4dB.

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AN EXPERIMENTAL DISTRIBUTED RESOLUTION OF WWW INTERACTIONS

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Likewise older Internet applications, such as Email and VoIP, the creation of greater number of WWW services make inevitable the occurrence of undesirable feature interactions.

The feature resolution on WWW must follow the basic constraints of Internet and, therefore, must be distributed.

In this paper we provide a brief introduction of feature interaction problem. Then, we depict one architecture to resolve the feature interactions and, finally, present an implementation of feature interaction resolution advisor based on deontic logics and Java.

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2004 - The 18th
European conference
on Solid-State
Transducers*

FINE-TUNING OF THE SPECTRAL COLLECTION EFFICIENCY IN MULTILAYER JUNCTIONS

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a-SiC:H/a-Si:H p-i-n/p-i-n tandem cells with different i-layer thickness have been produced by PECVD and tested for a proper fine-tuning of the spectral collection efficiency. The tandem structure takes advantage on the radiation wavelength selectivity due to the different light penetration depth inside the a-Si:H and a-SiC:H absorbers. The thickness and the absorption coefficient of the front p-i-n cell were optimized for blue collection and red transmittance and the thickness of the back one adjusted to achieve full absorption in the green and high collection in the red spectral ranges. Preliminary results show that device optimization for red detection can be obtained by reducing the thickness of the internal recombination junction while by increasing the intrinsic layer of the bottom a-Si:H cell, a better detection of the green color under appropriated applied voltages is foreseen.

The physics behind the device functioning is explained through a numerical simulation of the internal electrical configuration of the device in dark and under different wavelength irradiations. Considerations about conduction band offsets, electrical field profiles and inversion layers will be taken into account to explain the optical and voltage bias dependence of the spectral response. Experimental results about the spectral collection efficiency are presented and discussed from the point of view of the color sensor applications.

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September 2005-
Barcelona, Thin Solid
Films, Article in Press.*

AN AMORPHOUS SiC/Si IMAGE PHOTODETECTOR WITH VOLTAGE-SELECTABLE SPECTRAL RESPONSE

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The sensitive devices are multilayer stacked structures p-i-n/p-i-n based on a-SiC : H and a-Si : H between two transparent conductive contacts. The thickness and the absorption coefficient of the front p-i-n cell is optimized for blue collection and red transmittance and the thickness of the back one adjusted to achieve full absorption in the green and high collection in the red spectral ranges. Color discrimination is achieved through the modulation of one, two or both cell depletion regions by an applied external voltage.

The devices are characterized through the analysis of the photocurrent and spectral response under different steady state optical bias and applied voltages. In order to achieve full color discrimination and to evaluate the sensors responsivity to different light wavelengths, the photocurrent generated by a modulated red light is measured under different optical/electric bias. The sensor element is illuminated through the back diode with red modulated light and the optical bias applied onto the front diode.

From the experimental results it is observed that when using a red modulated light the thin a-SiC : H front absorber (200 nm) maximizes the conversion efficiency for blue front optical bias and the thickest back absorber layer (1000 nm) minimizes the conversion efficiency in the red range.

Results show that the conversion efficiency to a red modulated light under blue front optical bias is maximized when a 200 nm a-SiC : H front absorber is used, and minimized in the red range if the absorber layer of the back diode is around 1000 nm thick. In those devices the green photons absorption occurs mainly across the front diode, the n-p defective interface and at the front side of the back diode. Under reverse bias and blue irradiation the collection is high since the back diode becomes fully depleted due to its self-biasing process. Under red illumination the a-Si:H back absorber acts as a load due to the high light penetration depth of the red photons and the low collection is determined by the dark characteristics of the front diode. In the green spectral range the reverse bias increases the potential drop across the back diode and the collection increases linearly. The effect of the applied voltage on the color selectivity and spectral sensitivity is discussed and supported by a physical model based on a numerical simulation.

EXTENDING MOBILE PHONE USAGE FOR NON-CONVENTIONAL APPLICATIONS – WIRELESS IDENTIFIER

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The main purpose of this paper is to introduce some new non-conventional applications to allow the exploitation of today's mobile phone resources. These resources include digital cameras, IrDA, Bluetooth, speakers, microphones, etc.

The range of applications can go simply from obtaining information of the world around us, like in a museum getting a complete description of the item being analysed, as referred in the Cooltown project [1]. In this paper we'll explain an application that allows electronic payments, for example, buying products in a coffee shop or a corner vending machine without using coins or bills using only, the always present, cell phone. We detail an application running on a mobile phone that illustrates as phones can be used as an alternative form of payment or identification of a user. The achieved results, encountered challenges and possible solutions are presented.

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- International
Conference on
Electrical Engineering,
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Vol. 1, pp. 39,
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PROPRIEDADES ÓPTICAS E TRANSPORTE ELECTRÓNICO TRANSIENTE, RELACIONADOS COM A DESORDEM, EM SEMICONDUTORES DE GRANDE HIATO

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Publicado em:

Actas das "Jornadas de Engenharia de Electrónica e Telecomunicações e de Computadores" (ETCo5), 17 a 18 de Novembro 2005, ISEL, Lisboa, Portugal.

Neste trabalho estudamos as propriedades ópticas e o transporte electrónico em semicondutores de grande hiato, usando uma abordagem relacionada com a desordem estrutural frequentemente encontrada nestes materiais. Observamos uma variedade de características da fotocorrente transiente (TPC) e fotoluminescência transiente (TPL) que não podem ser explicados no âmbito dos mecanismos "canónicos" de relaxação electrónica, que são, para TPC, o modelo de Captura Múltipla (MT) de portadores livres e, para TPL, o modelo de recombinação entre pares de dadores e aceitadores (DAP) localizados. Em consequência, desenvolvemos um novo modelo analítico (Modelo TR) que integra a evidência experimental complementar de dispersão espacial (DAP) e dispersão energética (caudas das bandas). O modelo baseia-se na competição entre a termalização e recombinação (TR) de portadores minoritários capturados em estados energéticos, distribuídos exponencialmente em energia, e localizados no espaço. O modelo descreve a dependência da TPL da energia e do tempo, em excelente concordância com os dados experimentais, e revela a correlação entre TPL e TPC.

NON-LINEAR OPTICAL SPONTANEOUS PHOTOLUMINESCENCE EMISSION ENHANCEMENT EFFECT IN WIDE GAP GALLIUM NITRIDE THIN FILMS

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With two interfering pulses from the 4th harmonic of a Nd-YAG laser we burnt a periodic lattice structure into the surface of GaN thin films. The lattice period of this permanent grating could be controlled between less than one and several tens of microns. Above the decomposition threshold, nitrogen evades from the sample surface, and the residual metallic gallium accumulates in the form of tiny droplets at the surfaces.

The patterned structure shows structural similarities with microcavities. The question arises if the residual metallic gallium may act as a partially reflecting mirror.

To test this hypothesis, we studied the steady-state and transient photoluminescence through the modulation of light emerging from the ubiquitous broad “yellow” photoluminescence band. The microlattice shows up by energy-equidistant spontaneous emission enhancement peaks in the steady-state photoluminescence spectra. We suggest that the partial reflection due to the residual metallic gallium leads to the observed enhancement effect.

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A GLOBAL TRAINING ALGORITHM FOR RADIAL BASIS FUNCTIONS NEURAL NETWORKS

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Jornadas de Engenharia de Telecomunicações e Computadores (JETC'05), ISEL, Novembro de 2005.

Radial basis functions neural networks (RBFNN) are widely used for regression and classification problems. The topology of this neural network consists of an input layer, a hidden layer containing the radial basis functions and their centers, and an output layer performing the weighted sum of the values from the hidden layer. The classical training algorithms for RBFNN are divided into two separate stages. The first stage consists of an unsupervised algorithm to adjust the centers of the hidden layer. After the first stage is complete, the second stage is carried out by a (supervised) least squares algorithm to adjust the weights of the output layer. These algorithms simplify the training problem by dividing it into two separate simpler problems. This simplification has the shortcoming that there is no interaction and adjustment between these stages. In this work, we analyse the RBFNN as a mixture of Gaussians, considering that the radial basis functions, in the hidden layer, are Gaussians. We represent the Gaussian functions of the hidden layer by their mean vector and covariance matrix. This way, the RBFNN is treated as a global single model, to be trained globally. We derive an expectation-maximisation (EM) algorithm to learn the means and covariances of the Gaussian radial basis functions, from the training set. In each iteration of the EM algorithm, we simultaneously adjust the weights of the output layer by logistic regression. We exploit ways to combine EM and logistic regression algorithms. This way, the training of the RBFNN is performed with a global algorithm integrating EM and logistic regression. Our approach is tested and compared against the two-stage training algorithms, on synthetic and real data for binary classification problems. In our tests, the proposed algorithm achieved better performance with faster training, when compared to two-stage algorithms.

CIRCUITOS, SENSORES E ACTUADORES PARA DETECÇÃO REMOTA DE COMBOIOS

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Neste artigo descreve-se um sistema para a detecção remota de comboios, caracterizando-se a parte material que consubstancia a aplicação no terreno. Os circuitos transmissor e receptor, desenvolvidos de raiz, destinam-se à geração e à recepção dos trens de impulsos do sistema. Conjuntamente com estes circuitos, foram utilizados os transdutores adequados a cada uma das vertentes. Associado ao circuito de transmissão foi empregue um transdutor magnetoestrutivo que excita o carril com trens de impulsos gerados pelo transmissor. No que respeita ao receptor, este recebe o eco do carril através de um acelerómetro piezoelétrico. Serão descritos os circuitos que implementam os módulos de transmissão e de recepção, bem como as características dos transdutores associados a cada um deles. Por último, são considerados os aspectos da realização experimental no que toca à instalação dos transdutores no meio físico no qual decorreram os trabalhos de campo.

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 Jornadas de
 Engenharia de
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 Telecomunicações e
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 Lisboa, Portugal,
 Novembro 2005*

SIMULAÇÕES DE MOBILIDADE EM LISBOA PARA AVALIAÇÃO DE DESEMPENHO DE REDES MÓVEIS

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O realismo de um modelo de mobilidade é fundamental para a avaliação correcta do desempenho de uma rede de comunicações móveis. Muitas das vezes na literatura são usados modelos menos realistas motivados por razões de simplificação e diminuição da carga de processamento. Nesta comunicação, propomos um novo modelo de mobilidade para tráfego rodoviário mais próximo da realidade e aplicado à cidade de Lisboa.

O ponto de partida é a deslocação consciente dos condutores em grupo, evoluindo para o conceito de “smart travelling” ao mesmo tempo que é impulsionado pelo comportamento social dos condutores recolhido em inquéritos e medidas experimentais de tráfego. Foram efectuadas simulações para a cidade de Lisboa e os resultados estatísticos foram comparados com dados experimentais recolhidos de outros estudos efectuados para a Câmara Municipal de Lisboa.

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SIGE MONOLITHIC LNAS FOR LMDS

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In this paper the performance of BiCMOS $0,5\mu\text{m}$ SiGe QUBiC₄G technology to be used on a LNA for the LMDS service is presented. The best HBT for this purpose is selected. For this HBT and IC bias current leading to NF_{min}, simple LNAs were designed: common emitter with resistive and inductive bias; and cascode. The results show the possibility of using the QUBiC₄G technology, optimized for low microwave applications (few GHz), at the low millimeter wave band – NF_{ff}5dB, G_{ff}4dB per stage.

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*XX Conference on
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A 2.4GHZ MONOLITHIC CMOS DOWN-CONVERSION IMAGE REJECTION MIXER WITH INTEGRATED OSCILLATORS

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17-18 Novembro 2005,
Lisboa, 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 for low cost and high integration processing. Although a significant progress has been made in RF front-end designs using this technology, a great potential remains to explore since the presented solutions are still limited to a restricted number of wireless applications. 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. Very important key-parts in transceiver design that allows eliminating the off-chip components, to fully integration, are the mixer and the oscillators. Mixers and oscillators are found in all wireless communications systems.

This paper describes the design and simulation of a monolithic down converter image-rejection mixer integrated with oscillators. The fully integrated circuit was implemented in a 0.35 μ m CMOS standard technology. The simulations were performed with BSIM3 model and showed a 50dB image rejection. The mixer presents 14dB conversion gain at 2.4GHz for 1.8V power supply while all the circuit dissipating 18mW.

AMPLIFICADOR DE SINAL MONOLÍTICO CMOS A 1GHZ, 3V COM GANHO CONTROLADO DIGITALMENTE

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As comunicações sem fios suportam-se em tecnologias que têm vindo a evoluir de uma forma sem precedentes. Com a pressão do mercado dando ênfase à necessidade premente de implementação de circuitos electrónicos cada vez mais complexos, atendendo ao aumento de funcionalidades exigidas, mais leves, de menor custo e consumo reduzido, aumenta a necessidade de pesquisa de soluções inovadoras que permitam uma maior integração dos circuitos electrónicos.

Esta comunicação descreve o projecto e simulação de um amplificador de sinal monolítico com ganho variável controlado digitalmente. O circuito é constituído por dois blocos de amplificação e um módulo DAC. O módulo digital, com quatro bits de entrada, comanda o ganho do amplificador, actuando na transconductância dos dispositivos activos. O circuito, totalmente integrado, é implementado numa tecnologia CMOS normalizada de $0,35\mu\text{m}$ da AMS¹ (C35B4), ocupando uma área activa inferior a $0,01\text{mm}^2$.

As simulações foram obtidas usando o modelo BSIM3 e apresentam um ganho a variar entre um mínimo de -36dB e máximo de 28dB , com uma frequência de 1GHz e tensão de alimentação de 3V . O consumo do circuito, incluindo o bloco digital, é inferior a 5mW .

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ESTIMAÇÃO DE TRÁFEGO MISTO PARA UMTS

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This paper presents a set of traffic source models for UMTS traffic estimation. In order to estimate UMTS traffic, the city of Lisbon was used as reference scenario, where a set of twelve appropriated services were selected and three user profiles, were identified. All these data are crossed with Lisbon operational environments (classified by a local operator). After this process, it is possible to estimate the traffic density for UMTS, which is weighted by: user profile, service, operational environment and the total traffic volume. Being the total traffic volume, a very useful result, allowing the base stations localisation estimation. Additionally in this work, the impact of services and network general parameters into the UMTS network capacity is analysed. Based on these work, one can for example, estimate that for Lisbon (2006), 325 base stations are required to cover the UMTS traffic.

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Portugal,
Novembro 2005
(<http://www.deetc.isel.ipl.pt/jetco5/>)*

ANÁLISE DE DESEMPENHO DE TRANSACÇÕES SOBRE BLUETOOTH

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In this communication the Bluetooth standard is analyzed and used in applications with different characteristics than of the foreseen initially in the standard. The transmission of 128 bytes is the object in study, this transmission as to be made as quickly as possible since the terminals will be in movement at a high speed. The performance of this technology is analyzed using several connections that are created on different layers of the Bluetooth stack and using different versions of the standard. The main conclusions is that is possible to reduce the standard time necessary to establish the connections, thus allowing the establishment of fast transactions with one of the terminals in movement.

It was demonstrated that the transaction of 128 byte occur inside of a maximum window of 5 seconds, independently of the version of Bluetooth that is used in the receivers. To reduce the transaction time is needed to change the default values used in the standard, thus improving the time needed to research the devices and establish the connections.

Publicado em:

*Terceiras Jornadas de
Engenharia de
Electrónica e
Telecomunicações e
de Computadores
2005, Lisboa,
Portugal,
Novembro 2005
(<http://www.deetc.isel.ipl.pt/jetc05/>)*

OPTIMIZAÇÃO CELULAR EM UMTS-FDD

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Publicado em:

*Terceiras Jornadas de
Engenharia de
Electrónica e
Telecomunicações e
de Computadores
2005, Lisboa,
Portugal, Novembro
2005
(<http://www.deetc.isel.ipl.pt/jetco5/>)*

The planning and optimization process of an UMTS network is a complex task. In this paper some quasi optimal solutions for UMTS-FDD are presented. The system optimisation is accomplished using Artificial Intelligence algorithms which, are guided by some heuristics. For such, an UMTS-FDD network simulator was implemented and a cost function calculated for each simulation. This function evaluates the performance of the system, being used as an input to the optimisation algorithm and for its decisions. Based on a given reference scenario, the parameters that should be optimised are as follows: number of base stations, antennas height and its tilt angles.

Finally the main conclusion is that the UMTS network capacity it is strongly conditioned by the generated level of interference and the set of supported services.

MODELO DE PROPAGAÇÃO PARA WLANS

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WLANS are nowadays at the top of the mass market networks technologies. They are essentially implemented in indoor environments, where the traditional planning tools are not yet focused. Although the concerning to improve the radio planning quality, the existing propagation models can still be sharpened for better outcomes, mainly in large buildings. A new propagation model is proposed and evaluated with measurements at 2.4GHz and also a 3D planning tool is presented, with the ability to execute coverage and capacity analysis on indoor multi-floors environments. This new propagation model adapts itself to multiple indoor scenarios following the performed measurements.

Publicado em:

Terceiras Jornadas de Engenharia de Electrónica e Telecomunicações e de Computadores 2005, Lisboa, Portugal, Novembro 2005
(<http://www.deetc.isel.ipl.pt/jetc05/>)

RESOLUÇÃO DISTRIBUÍDA DE INTERACÇÕES DE SERVIÇOS NA INTERNET

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Publicado em:

*Proceedings of
"3^ª Jornadas de
Engenharia Electrónica
e Telecomunicações e
de Computadores"*

A proliferação da Internet levou ao crescimento substancial do número de serviços disponibilizados em aplicações como Email, VoIP e WWW, que conduziu à inevitável ocorrência de interacções, com comportamentos indesejáveis.

A resolução das interacções de serviços na Internet deve obedecer às características deste meio e como tal deve ter uma arquitectura distribuída. O projecto desenvolvido nesta dissertação apresenta uma solução baseada numa arquitectura distribuída, onde cada nó recorre à resolução prestada por um conselheiro [1].

Finalmente é apresentada uma proposta para a implementação do conselheiro com utilização de fórmulas deónticas e assente em tecnologia Java. O funcionamento da solução foi testado e adaptado com a aplicação de correio electrónico JAMES (Java Apache Mail Enterprise Server) da Apache Software Foundation (ASF).

Os resultados obtidos demonstraram o funcionamento da solução de acordo com os objectivos do projecto e o desempenho do sistema não comprometeu o nível de serviço da aplicação de Email.

MISTURADOR MONOLÍTICO A 2.4GHZ EM TECNOLOGIA CMOS 0.35μM USANDO CÉLULA DE GILBERT

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Esta comunicação visa apresentar um misturador duplamente equilibrado monolítico, para operar a 2.4 GHz, em tecnologia CMOS de 0.35μm usando como topologia básica a célula de Gilbert.

O misturador apresentado destina-se a funcionar como detector de fase numa Malha de Captura de Fase (PLL). O circuito utiliza transístores MOS e foi inicialmente projectado como misturador de dois sinais sinusoidais, analisando-se o ganho como misturador e a rejeição de espúrias na saída para verificar o funcionamento como circuito equilibrado. Seguidamente foi testado como detector de fase, apresentando na sua saída um sinal de erro proporcional à diferença de fase entre os dois sinais de entrada.

No desenho e simulação de desempenho do circuito utilizou-se o ambiente CADENCE, uma ferramenta de desenvolvimento de circuitos integrados bastante versátil, e o design-kit da Austria Micro Systems. A tecnologia utilizada é a CMOS standard de 0.35μm (C35B4) com 4 metais e 2 polys.

Publicado em:

*Jornadas de
Electrónica
Telecomunicações e
Computadores 2005*

OSCILADOR LC MONOLÍTICO COMANDADO POR TENSÃO A 2,4GHZ

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Publicado em:
*Jornadas de
Electrónica
Telecomunicações e
Computadores 2005*

Esta Comunicação tem como finalidade divulgar o projecto de um VCO monolítico a 2.4GHz para integrar uma Malha de Captura de Fase (PLL). O Oscilador projectado é baseado num par diferencial cruzado (parte activa). O circuito funciona com uma tensão de 2.8V e com uma tensão de comando entre 1.6V e 1.8V, produzindo uma variação de frequência entre 2.4GHz e 2.75GHz.

No desenho e simulação de desempenho do circuito utilizou-se o ambiente CADENCE, uma ferramenta de desenvolvimento de circuitos integrados bastante versátil, e o design-kit da Austria Micro Systems. A tecnologia utilizada é a CMOS standard de 0.35 μ m (C35B4) com 4 metais e 2 polys.

UMTS TRAFFIC ESTIMATION

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This paper presents a set of traffic source models for UMTS traffic estimation. In order to estimate UMTS traffic, the city of Lisbon was used as reference scenario, where a set of twelve appropriated services were selected and three user profiles, were identified. All these data are crossed with Lisbon operational environments (classified by a local operator). After this process, it is possible to estimate the traffic density for UMTS, which is weighted by: user profile, service, operational environment and the total traffic volume. Being the total traffic volume, a very useful result, that allows the estimation of base stations localisation. Additionally in this work, the impact of services and network general parameters into the UMTS network capacity is analysed. Based on these work, one can for example, estimate that for Lisbon (2006), 325 base stations are required to cover the UMTS traffic.

Publicado em:

*Jetc2005 – Jornadas
de Eng. de Electrónica
e Telecomunicações e
de Computadores, 17-
18 Novembro 2005,
Lisboa, Portugal.*

PERSONAL UNIFIED COMMUNICATIONS

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Publicado em:
Volume 117, 18
November 2005, Page
47, Third Workshop in
Electronics,
Telecommunications,
and Computer
Engineering

The project PUC, “Personal Communication System for next generation telecommunications networks”, integrates, in the same platform, a set of personal communication services, namely, web mail service and instant message service. The supporting application platform is the JBoss, a J2EE complying product. The services were implemented in order to guarantee the independence of terminal type access (the access can be made by a Web terminal, voice, WAP or another). This paper presents the developed work according to mainly an engineering perspective, focusing the implementation details which had greater relevance, namely the description of the problems, of the adopted and implemented solutions, discussing the advantages and the disadvantages of those same solutions and finally proposing alternative solutions.

REPETIDOR PARA AMBIENTES INTERIORES EM CDMA2000

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This article describes a CDMA2000 indoor repeater for the 460MHz band. The prototype is meant to be connected between two antennas, thus providing amplification in both directions. At the end it was tested in field, where it showed a good increase in the indoor signal strength..

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*JETC'05, Third
Workshop in
Electronics,
Telecommunications,
and Computer
Engineering*

RACIOCÍNIO ADAPTATIVO DE BASE EMOCIONAL EM AGENTES INTELIGENTES

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Publicado em:

*Actas das Terceiras
Jornadas de
Engenharia de
Electrónica e
Telecomunicações e
de Computadores,
ISEL, 2005.*

O projecto e implementação de agentes inteligentes capazes de comportamento eficaz em ambientes reais, onde a incerteza e o dinamismo são generalizados e onde tempo e recursos são limitados, levanta problemas importantes, relacionados quer com a capacidade adaptativa dos agentes, quer com a complexidade computacional dos processos cognitivos envolvidos, em particular de processos de raciocínio e planeamento. Neste artigo são apresentados mecanismos de base emocional que tornam possível a adaptação a ambientes dinâmicos e um uso controlado de recursos, através da focagem dos processos cognitivos. No sentido de avaliar a abordagem proposta são apresentados resultados experimentais em comparação com resultados de outras abordagens de referência.

IMPERIAL COLLEGE AT TRECVID

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We describe our experiments for the shot boundary detection, high-level feature extraction and search. In the shot boundary detection task, we employ our proven method based on the calculation of distances between colour histograms of frames over a range of timescales. For the search task, we tested a different system. This year, content based search is complemented with a new relevance feedback method. Results of one interactive run are presented to evaluate the performance of the new system. In the high-level feature detection task we tested two new methods: naïve model and non-parametric density estimation. We evaluated these models with all keywords.

Publicado em:

*TREC Video Retrieval
Evaluation (TRECVID),
Gaithersburg, MD,
Nov., 2005*

EMOTION BASED ADAPTIVE REASONING FOR RESOURCE BOUNDED AGENTS

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In the design of resource bounded agents, high-level cognitive activities, such as reasoning, raise important problems related both to the adaptive ability and to the computational complexity of the underlying cognitive processes. To address these problems, we adopt an agent model where emotion and cognition are conceived as two integrated aspects of intelligent behavior and we present affective-emotional mechanisms that support the adaptation to changing environments and a controlled use of resources. These mechanisms produce an attention field that constrains the input to reasoning processes and also regulate the activation period of those processes. Experimental results are presented to illustrate this approach and to evaluate it by comparison with reference results concerning intention reconsideration policies.

Publicado em:

Proceedings of the 4th International Joint Conference on Autonomous Agents and Multi-Agent Systems, ACM Press, 2005, Pages 921-928.

ESTIMAÇÃO DO SUBESPAÇO DE SINAL EM DADOS HIPERESPECTRAIS

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A redução de dimensionalidade é uma tarefa crucial no processamento e análise de dados hiperespectrais. Esta comunicação propõe um método de estimação do subespaço de sinal baseado no erro quadrático médio. O método consiste em primeiro estimar as matrizes de correlação do sinal e do ruído e em segundo seleccionar o conjunto de vectores próprios que melhor representa o subespaço de sinal. A eficiência deste método é ilustrada em imagens hiperespectrais sintéticas e reais.

Publicado em:

*Proceedings of the 3rd
Jornadas de
Engenharia de
Electrónica e
Telecomunicações e
de Computadores,
2005*

SISTEMA DE IDENTIFICAÇÃO BASEADO EM FACES

**Calado, B.; Murteira, L.; Mendes, Jorge P.;
Abrantes, A.**

Electronics Telecommunication and Computer Department ISEL,
Lisbon, Portugal

Publicado em:

*Terceiras Jornadas de
Engenharia de
Electrónica e
Telecomunicações e
de Computadores, 17
e 18 de Novembro de
2005, Lisboa, Portugal*

Este artigo descreve um sistema de detecção e reconhecimento de faces humanas. O sistema processa imagens estáticas, sequências de vídeo guardadas em disco ou sequências de vídeo captadas com uma câmara Web. O sistema realiza o reconhecimento, detectando em primeiro lugar a localização das faces na imagem. A Detecção de Faces é decomposta em dois níveis. O primeiro nível envolve a detecção da face na imagem, ao passo que o segundo nível tem por objectivo detectar e localizar a posição dos olhos apenas em algumas regiões da imagem (aquelas consideradas candidatas a faces). Após a fase de detecção surge um bloco de Reconhecimento, onde foi utilizado o método de análise em componentes principais (*Principal Component Analysis – PCA*). Para avaliar o sistema de reconhecimento de faces proposto neste trabalho, foi utilizada a base de dados da FERET (*Face Recognition Technology*) e outra criada no âmbito deste trabalho denominada ISEL.

DESIGN METHOD FOR INTEGRATED CMOS QUASI-SQUARE-WAVE DC-DC CONVERTERS

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This paper presents a first study of resonant converter topologies targeted for CMOS integration. A new method to design very-high frequency (MHz) switching Quasi-Square-Wave converters with the objective of CMOS implementation is presented.

Similar work has been developed using hard-switching techniques, but the high-speed and low-voltage applications, nowadays, require high dynamic response, high-efficiency and minimum footprint. These demands force the switching frequency to increase to several MHz, leading to higher losses. Maintaining high efficiency at high switching frequency is a major challenge. Among the Power Electronics DC-DC converters circuit topologies, the soft-switching topologies are distinguished by their efficiency and low Electromagnetic Interference (EMI). Thus, the use of soft-switching techniques appears attractive to minimize noise and switching losses.

Simulation work based on a 0,35mm CMOS process device modelling revealed distinct problems for this soft-switched Quasi-Square-Wave topology, when compared to the discrete implementation. A ZVS QSW buck converter was designed using the proposed method for a switching frequency in the range of hundreds of MHz. Future work directions are pointed out according to the identified problems.

Publicado em:

*DCIS 2005, XX
Conference on Design
of Circuits and
Integrated Systems:
CD-ROM, 23-25
November 2005,
Lisboa, Portugal*

ADAPTATION AND DECISION-MAKING DRIVEN BY EMOTIONAL MEMORIES

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The integration between emotion and cognition can provide an important support for adaptation and decision-making under resource-bounded conditions, typical of real-world domains. The ability to adjust cognitive activity and to take advantage of emotion-modulated memories are two main aspects resulting from that integration. In this paper we address those issues under the framework of the agent flow model, describing the formation of emotional memories and the regulation of their use through attention focusing. Experimental results from simulated rescue scenarios show how the proposed approach enables effective decision making and fast adaptation rates in completely unknown environments.

Publicado em:

*Proceedings of the
12th Portuguese
Conference on
Artificial Intelligence,
LNCS 3808, Springer-
Verlag, 2005, Pages
102-114.*

MAGNETORESISTANCE DUE TO DOMAIN WALLS IN SEMICONDUCTING MAGNETIC NANOSTRUCTURES

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Magnetoresistance of a semiconducting ferromagnetic nanostructure with a laterally constrained domain wall is analyzed theoretically in the limit of sharp domain walls and fully polarized electron gas is considered. The spin-orbit interaction of Rashba type is included into considerations. It is shown that the magnetoresistance in such a case can be relatively large, which is in a qualitative agreement with recent experimental observations. It is also shown that spin-orbit interaction can enhance the magnetoresistance. The role of localization corrections is also briefly discussed.

(c) 2005

Publicado em:

Materials Science and Engineering C
Volume 25, Issue 5-8,
December 2005, Pages
705-709

A REAL-TIME COLOUR AND IMAGE PROCESSING P-I-N/P-I-N DEVICE WITH OPTICAL READOUT

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A two-terminal, optically addressed image processing device based on two stacked sensing/switching p-i-n a-SiC:H diodes is presented. The charge packets are injected optically into the p-i-n sensing photodiode and confined at the illuminated regions, locally changing the electrical field profile across the p-i-n switching diode. A red scanner is used for charge readout. The various design parameters and addressing architecture tradeoffs are discussed. The influence on the transfer functions of an a-SiC:H sensing absorber, optimized for red transmittance and blue collection or of a floating anode in-between, is analysed. Results show that the thin a-SiC:H sensing absorber confines the readout to the switching diode and light filters the structure, allowing full colour detection at two appropriated voltages. When the floating anode is used the spectral response broadens, allowing B&W image recognition with improved light-to-dark sensitivity. A physical model supports the image and colour recognition process.

LARGE AREA P-I-N IMAGE SENSITIVE DEVICES DEPOSITED ON PLASTIC SUBSTRATES

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Large area p-i-n image sensors deposited on plastic substrates were produced at low temperatures (110°C) by PE-CVD and compared with similar sensors deposited on glass substrates. The same sensing element structure ZnO:Al/p(SiC:H)/i(Si:H)/n(SiC:H)/Al was used for both devices. In this work, the efforts are focused mainly on the optimization of the output characteristics of the sensor when fabricated on plastic substrates. The role of the sensor configuration and readout parameters on the image acquisition process is analyzed. The optical-toelectrical transfer characteristics show a reasonable quantum efficiency under a red light pattern, broad spectral response, and reciprocity between light and image signal. First results show that the sensors deposited on a flexible substrate present smaller light to dark sensitivity than those deposited on glass. In both, the non-ohmic behavior of the transparent conductive oxide front contact blocks the carrier collection and leads to a surprising linear dependence of the image signal with the applied voltage.

Publicado em:

Revista Mexicana de Física 52 (2 SUPPL.), pp. 57-60.

THIN FILM SENSORS PRODUCED AT LOW TEMPERATURE: A TRADE-OFF BETWEEN CARBON COMPOSITION AND SPECTRAL RESPONSE

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A series of large area single layers and homo and heterojunction cells in the assembly glass/ZnO:Al/p ($\text{Si}_x\text{C}_{1-x}\text{H}$)/i (Si:H)/n ($\text{Si}_x\text{C}_{1-x}\text{H}$)/Al ($0 < x < 1$) were produced by PECVD at low temperature. Junction properties, carrier transport and photogeneration are investigated from dark and illuminated current-voltage characteristics, and spectral response measurements in dark and under different illumination conditions. For the heterojunction cells atypical J-V characteristics under different illumination conditions are observed leading to poor fill factors. High series resistances around $10^6 \Omega$ were measured. In these structures it was observed that the responsivity decreases with the increase of the light bias intensity. The homojunction presents the typical behaviour of a non optimized p-i-n cell and the responsivity varies only slightly with the light bias conditions.

Publicado em:

*Revista Mexicana de
Física Volume 52,
Issue 2 SUPPL., Pages
32-35*

TEMPORAL PATTERNS OF TV WATCHING FOR PORTUGUESE VIEWERS

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Audiometer systems provide enormous amounts of detailed TV watching data. Several relevant and interdependent factors may influence TV viewers' behavior. In this work we focus on the time factor and derive Temporal Patterns of TV watching, based on panel data. Clustering base attributes are originated from 1440 binary minute-related attributes, capturing the TV watching status (watch/not watch). Since there are around 2500 panel viewers a data reduction procedure is first performed. K-Means algorithm is used to obtain daily clusters of viewers. Weekly patterns are then derived which rely on daily patterns. The obtained solutions are tested for consistency and stability. Temporal TV watching patterns provide new insights concerning Portuguese TV viewers' behavior.

Publicado em:

2005 Portuguese Conference on Artificial Intelligence, Volume 1, 05 December 2005, Pages 151-158, IEEE, ISBN 0-7803-9365-1

DE PROCESSOS INTERORGANIZACIONAIS CBPEL PARA PROCESSOS BPEL

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1 ISEL/DEETC

2 IST/INESC-ID

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Engenharia de
Electrónica e
Telecomunicações e
Computadores
(JETCo5), Novembro
de 2005, Lisboa,
Portugal*

A Common Business Process Execution Language (CBPEL) é uma nova especificação para a descrição de processos interorganizacionais descritos de forma global e única, e baseados em Web Services. A grande vantagem da utilização de uma descrição global e única consiste na possibilidade da geração automática dos processos das organizações participantes. Essa automatização tem por principal objectivo a redução do risco da concepção de processos interorganizacionais inconsistentes. Contudo até este momento não existe nenhum trabalho que apresente uma metodologia para a geração automática dos processos participantes. Este trabalho visa precisamente preencher essa lacuna promovendo uma reflexão sobre essa transformação, e apresentando um conjunto de regras para a sua automatização. A linguagem escolhida como destinatário da transformação foi a Business Process Execution Language (BPEL), uma vez que é a linguagem base da linguagem CBPEL.

CBPEL – LINGUAGEM PARA DEFINIÇÃO DE PROCESSOS DE NEGÓCIO INTERORGANIZACIONAIS

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Têm emergido recentemente várias linguagens XML para descrever processos de negócio, nomeadamente: BPEL, WSCI, XLANG, ou BPML. Contudo, estas linguagens são inadequadas para descrever processos de negócio interorganizacionais, que são processos com vários participantes em que o controle de execução é partilhado por todos. Para processos com estes requisitos poderia utilizar-se as linguagens WSCDL ou BPSS/ebXML, mas que apresentam algumas limitações na sua utilização. Este trabalho visa propor uma linguagem para modelar processos de negócio interorganizacionais, baseada nos conceitos da linguagem BPEL, à qual designamos por CBPEL (Common Business Process Execution Language).

Publicado em:

3a Conferência Nacional XML: Aplicações e Tecnologias Associadas (XATA 2005), Fevereiro de 2005, Braga, Portugal

TIME SEGMENTED SWEEP SINE TECHNIQUE FOR SNR ENHANCEMENT

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Publicado em:
*Forum Acusticum-
2005- CDROM
Proceedings*

The Swept Sine technique for the measurement of room impulse responses has advantages due to its large signal-to-noise ratio (SNR) and immunity against the time-variance of the DUT. The test signal used for the evaluation of the RIR corresponds to a set of M Swept Sine frames. Instead of directly applying the averaging technique, a weighting procedure can be used in order to improve the SNR even more. This method consists in splitting each captured Swept Sine frame into N segments. Beside this procedure, each segment is filtered by a filter bank, which splits the audio spectrum into multiple sub-bands. The energy within each sub-band is computed. This procedure ensures that the resulting Swept Sine signal has the highest SNR value. The main disadvantage of this kind of technique concerns the measurement time duration and is related to the number of sweeps in each set. For high background noise levels, the SNR can be very low, and the acoustical measurements will yield unreliable results for sound insulation, reverberation time and amplitude frequency response. If the classic Swept Sine technique is to be used, the averaging technique must then be applied to improve the SNR and consequently rising the measurement time. In this situation, the use of this new approach could be advantageous.

TIME SEGMENTED SWEPT SINE TECHNIQUE FOR ROOM IMPULSE RESPONSE ESTIMATION

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Coelho, J.L. Bento³

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The Swept Sine technique is becoming a popular technique for the measurement of room impulse response due to its large signal-to-noise ratio (SNR) and immunity against the time-variance of the room under test.

This new technique, named Time Segmented Swept Sine, consists in exciting the room with a set of M Swept Sine signal and applying a weighting average method.

For the measurement of the room impulse response (RIR) in the presence of high level non-stationary background noise the mean square of the overall sequence must be minimized in order to increase the SNR.

This method consists in dividing each Swept Sine signal into N segments followed by the estimation of the mean square (MS) value of the respective segment. A weighting procedure is applied to each segment followed by the average technique. This procedure ensures that the resulting Swept Sine signal has the highest SNR value.

Several examples are presented to compare the classic Swept Sine and the Time Segmented Swept Sine techniques, give advantages and disadvantages of each technique.

Publicado em:
*International Congress
on Sound and
Vibration - ICSV12-
2005- CDROM
Proceedings*

SISTEMA ELECTRÓNICO DE CONTROLO DE TEMPERATURA DA ÁGUA PARA APLICAÇÕES DOMÉSTICAS

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Este artigo descreve um sistema que permite controlar a temperatura e regular o caudal das águas sanitárias num ambiente doméstico. O sistema tem como limite sete saídas independentes de caudal, substituindo as tradicionais torneiras mecânicas e manuais. A arquitectura do sistema está dividida em dois tipos de blocos: a interface com o utilizador (IU) e o bloco de controlo e regulação (CR). A IU é composta por um mostrador e por um teclado que permitem a interacção do utilizador com o sistema. O bloco de CR é constituído por um circuito electrónico que gere os módulos da IU e o sistema electromecânico. No controlo de temperatura é usado um controlador PID digital. A regulação do caudal de cada saída é efectuada de forma independente.

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INFORMATION THEORETIC TEXT CLASSIFICATION USING THE ZIV-MERHAV METHOD

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Most approaches to text classification rely on some measure of (dis)similarity between sequences of symbols. Information theoretic measures have the advantage of making very few assumptions on the models which are considered to have generated the sequences, and have been the focus of recent interest. This paper addresses the use of the Ziv-Merhav method (ZMM) for the estimation of relative entropy (or Kullback-Leibler divergence) from sequences of symbols as a tool for text classification. We describe an implementation of the ZMM based on a modified version of the Lempel-Ziv algorithm (LZ77). Assessing the accuracy of the ZMM on synthetic Markov sequences shows that it yields good estimates of the Kullback-Leibler divergence. Finally, we apply the method in a text classification problem (more specifically, authorship attribution) outperforming a previously proposed (also information theoretic) method.

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VISUALIZATION IN LEARNING MATHEMATICS WITH HYPERVIDEO

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Visualization has always been an essential aid in the communication of mathematics. It is an important way to concretize concepts, to develop abstraction skills, and to motivate learning, for example in topology and geometry, and in the application of numerical methods to simulations of the real world. Video has proven to be one of the most adequate ways to communicate visualization results, allowing to present in a rich cultural context a large quantity and diversity of information in a brief period of time. However, by itself, video has a limited capability to support learning. The structure and interaction introduced by hypervideo allow providing the user with greater control and autonomy, exploring links among the information conveyed by the video and complemented by other materials, augmenting its capabilities as a cognitive artifact. This paper develops these ideas, presenting The Story of Pi hypervideo as a case study.

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<http://envc2005.multimeios.pt/Envc'2005> - Encontro Nacional de Visualização Científica, Centro Multimeios, Espinho, 17 Setembro 2005.



03

ENGENHARIA MECÂNICA

Anuário Científico 2005

ISEL

NITINOL – A NEW MATERIAL FOR BIOMEDICAL APPLICATIONS

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The present work surveys some of the more recent studies performed on the chemical and physical properties of NiTi alloys (Nitinol), aiming at its use as a biomaterial. On this basis, the shape memory effect is examined, as well as the corrosion resistance of the alloy when in contact with the human fluids, both under static and dynamic conditions. It is concluded that, in spite of the enhanced mechanical behaviour, which makes the material suitable for a wide range of medical applications, the results on the corrosion resistance and biocompatibility of the alloy are still not conclusive. Therefore, more information should be collected on the corrosion behaviour of the material, giving special attention to Nitinol used under stress, after deformation and under loading/unloading conditions, to avoid the lack of predictability on the corrosion behaviour of this alloy under dynamic conditions.

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PROMOÇÃO DE UMA APRENDIZAGEM ACTIVA NA DISCIPLINA DE TERMODINÂMICA

Carvalho, Isabel S.

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de 2005.*

No âmbito da Disciplina de Termodinâmica II do Curso de Engenharia Mecânica está a ser realizada uma experiência piloto com recurso à utilização de Simuladores com o objectivo de promover uma aprendizagem activa que conduza a uma maior responsabilização por parte dos alunos no processo de aprendizagem. A disciplina tem um curriculum tradicional com aulas Teóricas e Teórico-Práticas e uma componente Laboratorial reduzida. O curriculum inclui temas como Ciclos de Turbina, Ciclos de Motores Alternativos, Combustão, Psicrometria e Ciclos Frigoríficos e de Bombas de Calor. Os temas propostos para a elaboração de experiências virtuais são os seguintes: Fundamentos, Ciclos de Turbina, Motores Alternativos e Combustão. Numa fase inicial, os alunos são informados sobre os objectivos e procedimentos sendo-lhes facultado um conjunto de URLs com os Simuladores a utilizar. O acompanhamento deste trabalho é efectuado durante as aulas Teórico-Práticas devendo os alunos elaborar um relatório sobre cada tema proposto. No final são distribuídos aos alunos questionários sobre o trabalho realizado sendo-lhes solicitada a sua opinião sobre a utilização dos Simuladores assim como qual a sua contribuição para a aquisição de conhecimentos.

ALTERNATIVE ANODISING PROCESSES FOR ALUMINIUM AND 2024 ALUMINIUM ALLOY

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Belo, M. Da Cunha¹; Moura e Silva, T.²;
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The aim of this work is to show progresses reached with an alternative anodising process for aluminium and aluminium alloys, 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. The results obtained indicate 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.

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*CD de Comunicações e
Actas do CORROSION 2005 -
International
Conference "Science
and Economy",
Varsóvia, Polónia
(Junho 2005)*

SOME TOOLS AND METHODOLOGIES TO INCREASE STUDENTS INTEREST ON ENERGY AND ENVIRONMENT RELATED TOPICS

Carvalho, Isabel S.

Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal

Publicado em:

Proceedings of the 33rd SEFI Annual Conference - Engineering Education at the Cross-Roads of Civilizations, Ankara, Turkey, 7-10 de Setembro de 2005.

Several tools and methodologies are presented in order to promote active learning in different Engineering subjects, hence providing a wider choice and opportunity for students learning. Students are confronted with the less traditional ways of learning, like the traditional “knowledge acquisition” and “spoon-fed” subjects, which will lead them to paths like “problem based learning” and “learning by doing”. The tools and methodologies include the use of Simulators, Didactic Software, Web based high quality and rich contents, Virtual Libraries, online work and co-operative and collaborative working environments (either face-to-face or online). These tools and methodologies seek to give students more responsibility as well as to increase students’ engagement in the learning process.

A NEW MATERIAL FOR NEURAL STIMULATING PROSTHESES

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The last few decades have seen the development of electronic devices for chronic stimulation of the nervous system. Among them are the neural stimulating electrodes, used to replace or supplementing lost functions in the neurological handicapped, such as treatment of spinal injury, epilepsy or auditory disorders. Artificial stimulation of the nervous system requires the transfer of a certain amount of charge from the implanted electrodes to the nerve cells, which can be accomplished by electrochemical processes occurring at the electrode/solution interface. Progress in these devices are therefore dependent on the provision of new and more efficient materials capable of transfer high values of charge and that allow for miniaturization of the implanted electrodes in order to enhance selectivity in neuronal activation. This work aims at preparing a new material, to be used as neural stimulating devices that combine these two characteristics. For that purpose Ir was ion implanted on Ti-6Al₄V alloy and the material was subsequently surface enriched in Ir by chemical etching. The enrichment process was controlled by Auger depth profile and the charge injection capability of the material was assessed by cyclic voltammetry. It was found out that this new material combines the good charge storage properties of iridium with the mechanical properties of the titanium alloy, therefore making it prone to be used as neural stimulating electrode.

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*CD de Comunicações e
Actas do Congresso
Europeu de Corrosão
"Eurocorr 2005" p.
584, 4-8 de Setembro
2005, Lisboa, Portugal*

APRENDIZAGEM ACTIVA: AUDITORIA ENERGÉTICA

Carvalho, Isabel S.

Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal

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Moçambique, 3o
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de 2005.*

No âmbito de uma disciplina do 5o ano do Curso de Engenharia Mecânica promove-se a aprendizagem activa, i.e., “aprender fazendo”. Numa disciplina de curriculum tão vasto e abrangente (Utilização Racional de Energia, Cogeração, Gás Natural, Eólica, Solar, Biomassa, Nuclear, Hidrogénio entre outros) é proposto aos alunos a elaboração de um trabalho temático (em grupo), a desenvolver em ambiente colaborativo, e de um trabalho individual na área da Auditoria Energética. É sobre este último que o presente artigo se irá debruçar.

Após uma introdução ao tema é fornecido aos alunos um ficheiro em Excel (elaborado pelo professor) e um conjunto de informações e procedimentos para a realização da Auditoria. O local a auditar é a casa/apartamento dos próprios alunos. A folha de cálculo inclui quatro áreas de preenchimento obrigatório: Identificação, Caracterização do Local, Leituras e apresentação da informação na forma gráfica. No fim do semestre cada aluno apresenta o seu próprio caso estudado, assim como uma análise dos resultados e medidas que propõe de modo a conduzir a uma melhor Utilização Racional de Energia.

Toda a informação e estrutura do processo será detalhadamente apresentada, assim como quais os resultados obtidos e questões específicas existentes. Pode considerar-se que a sensibilização dos formandos (aproximadamente 100 alunos) para as questões energéticas, em particular a da Utilização Racional de Energia foi conseguida com sucesso, sendo apresentadas as medidas correctivas propostas assim como alguns dos casos de maior interesse.

SEMICONDUCTOR ELECTROCHEMISTRY APPROACH TO PASSIVITY AND STRESS CORROSION CRACKING SUSCEPTIBILITY OF STAINLESS STEELS

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The susceptibility of AISI 304 type stainless steel to stress corrosion cracking (SCC) in boiling concentrated boric acid-chloride aqueous solutions, appears closely linked to the formation of a chromium rich passive oxide film presenting a p-type semiconductivity. Furthermore, the flat band potential of the oxide, which separates potential regions of predominant ionic conduction from regions of predominant electronic conduction, can be considered a critical potential. A band structure model is proposed, in which the initiation of the SCC phenomenon can be described as being the consequence of a localised change of the semiconductivity properties of the passive film, promoted by dislocations, in the potential region situated near the flat band potential. Also a short discussion is presented focusing on the relation between the SCC and the corrosion potential and the electronic structure of the passive film.

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5076–5082

PROMOÇÃO DE UMA APRENDIZAGEM ACTIVA NA DISCIPLINA DE TERMODINÂMICA

Carvalho, Isabel S.

Departamento de Engenharia Mecânica, ISEL, Lisboa, Portugal

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Moçambique, 3o
Agosto -1 Setembro de
2005.*

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Os temas propostos para a elaboração de experiências virtuais são os seguintes: Fundamentos, Ciclos de Turbina, Motores Alternativos e Combustão. Numa fase inicial, os alunos são informados sobre os objectivos e procedimentos sendo-lhes facultado um conjunto de URLs com os Simuladores a utilizar. O acompanhamento deste trabalho é efectuado durante as aulas Teórico-Práticas devendo os alunos elaborar um relatório sobre cada tema proposto. No final são distribuídos aos alunos questionários sobre o trabalho realizado sendo-lhes solicitada a sua opinião sobre a utilização dos Simuladores assim como qual a sua contribuição para a aquisição de conhecimentos.

SIMULAÇÃO NUMÉRICA DE ELEMENTOS CURVOS FEITOS DE MATERIAIS COMPÓSITOS

Leite, Afonso; Navarro, Pedro; Travassos, João

ISEL, Departamento de Engenharia Mecânica, Lisboa, Portugal

O objectivo deste trabalho é fazer um estudo numérico de vigas ou elementos curvos em materiais compósitos, no programa ANSYS 8.1. Os elementos curvos foram simulados com elementos de casca multicamada (linear layered structural shell - SHELL99); elementos sólidos (3-D 8-Node Layered Structural Solid – SOLID46) e elementos planos 2D (2-D 8-Node Structural Solid – PLANE82), de modo a validar um modelo analítico. O modelo analítico foi baseado na teoria multicamada de Ko e Jackson (NASA). O material usado para fabricar os elementos curvos foi a fibra de vidro, sob a forma unidireccional, pré-impregnada com resina epoxídica, e com a seguinte sequência de empilhamento $[45/0/45/0_2/45/0]_5$. É feita uma comparação entre os três modelos numéricos, o modelo analítico e o ensaio experimental.

Publicado em:

Apresentado na 1ª CONFERÊNCIA IBÉRICA DE USUÁRIOS DE ANSYS, organizada pela Ingegiber, publicado no CD-ROM de apresentações do encontro, 03 a 04 de Novembro de 2005, Hotel Holiday Inn, Madrid, Espanha.



Figura 1 – Tensão radial máxima obtida a meio da espessura do elemento curvo.

CONSTRUÇÃO E MANUTENÇÃO DE GASODUTOS DE GÁS NATURAL EM REDES DE TRANSPORTE A ALTA PRESSÃO

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³ Dept. de Eng. Mecânica da UA, Universidade de Aveiro

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⁵ Direcção de ID do ISQ, Instituto de Soldadura e Qualidade - ISEL

O gás natural constitui uma fonte energética natural de elevado valor. O seu transporte é normalmente efectuado por redes de tubo soldados e enterrados. Estas redes exigem um programa de manutenção em que se incluem entre outras, operações de vigilância quanto a deformações inadmissíveis, resultando por exemplo de cargas de superfície. Os esforços suportados pelos tubos são geralmente complexos, na maior parte dos casos de modelação numérica difícil, principalmente resultando de combinações de cargas radiais e pressão interna podendo determinar a perda de estabilidade estrutural da tubagem. As cargas radiais podem resultar da passagem acidental superior de veículos pesados. Neste trabalho desenvolveu-se uma metodologia de simulação experimental do efeito de cargas de superfície numa tubagem soldada enterrada, que caracteriza o Gasoduto da Transgás. A medição do estado de deformação consistiu na extensometria eléctrica pela sua fiabilidade e precisão nos resultados.

Publicado em:

Publicado no proceedings do 4º congresso Luso-Moçambicano de Engenharia

DESENVOLVIMENTO DE ELEMENTOS CURVOS EM MATERIAIS COMPÓSITOS

Travassos, J.; Leite, A.; Simões, C.

ISEL, Departamento de Engenharia Mecânica, Lisboa, Portugal

Esta comunicação tem como objectivo apresentar o trabalho efectua- do na Secção de Projecto Mecânico do Departamento de Engenharia Mecânica do ISEL no seguimento de uma bolsa de investigação do Instituto Politécnico de Lisboa. Foi realizada uma revisão bibliográfica sobre elementos curvos em materiais compósitos de modo a adaptar um modelo analítico, um modelo numérico (Ansys 8.0) e modelos físicos para experimentação. O modelo analítico foi baseado na teoria multicamada de Ko e Jackson (NASA). O material usado para fabricar os elementos curvos foi a fibra de vidro, sob a forma unidireccional, pré-impregnada com resina epoxídica, e com a seguinte sequência de empilhamento $[45/0/45/0_2/45/0]_5$. O processo utilizado na fabricação dos elementos curvos foi o de autoclave com saco de vácuo e molde macho. O molde macho foi produzido a partir de um bloco de resina maquinável, curado em autoclave.

Publicado em:

Artigo apresentado no 4.^o Encontro Nacional do Colégio de Engenharia Mecânica da Ordem dos Engenheiros, publicado no CD-ROM de actas do encontro, 01 a 04 de Junho de 2005, Ordem dos Engenheiros, Lisboa.

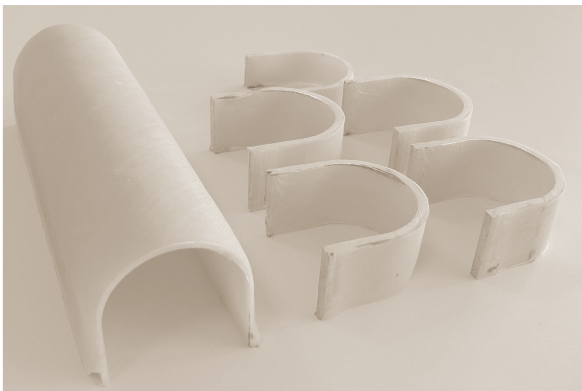


Figura 2 – Elementos curvos fabricados no autoclave laboratorial.

UM PROCEDIMENTO EXPERIMENTAL PARA A CARACTERIZAÇÃO DOS ESFORÇOS EM TUBAGENS SOLDADAS ENTERRADAS, SUJEITAS A CARGAS ACIDENTAIS NA SUPERFÍCIE.

Soares, J.A.R.¹; Ferreira, L.A.A.²; Melo, F.J.Q. de³;
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- 5 Direcção de Operação e Manutenção da TRANSGÁS Portugal

As tubagens soldadas enterradas, suportam esforços complexos, na maior parte dos casos de modelação numérica difícil, principalmente resultando de combinações de cargas radiais e pressão interna podendo determinar a perda de estabilidade estrutural da tubagem. As cargas radiais podem resultar da passagem superior de veículos pesados. Neste trabalho desenvolveu-se uma metodologia de simulação experimental do efeito de cargas de superfície numa tubagem soldada enterrada, que caracteriza o Gasoduto da Transgás. A medição do estado de deformação consistiu na extensometria eléctrica pela sua fiabilidade e precisão nos resultados. Aplicando posteriormente modelação numérica em 3D, com o programa de cálculo estrutural ANSYS 5.4.

Publicado em:

Publicado no livro de actas da 6º congresso nacional mecânica experimental APAET- Universidade dos Açores de 27 a 29 de Julho de 2005



ENGENHARIA QUÍMICA

Anuário Científico 2005

ISEL

CHARGE DENSITY WAVE TO MIXED DENSITY WAVE PHASE TRANSITION AT HIGH FIELDS IN $(\text{PER})_2\text{M}(\text{mnt})_2$ ($\text{M} = \text{Au}, \text{Pt}$)

Graf, D.¹; Choi, E.S.¹; Brooks, J.S.¹; Dias, J.C.²; Henriques, R.T.²; Almeida, M.²; Matos, M.³; Rickel, D.³

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Low-dimensional organic systems have been an area of keen interest over the last two decades due to the rich phase diagrams found by manipulating the parameters of temperature, pressure and applied field. Among these organic systems, the quasi-one-dimensional (Q1D) system $(\text{Per})_2\text{M}(\text{mnt})_2$, (where $\text{M} = \text{Au}$ and Pt) undergoes a lattice distortion below 12 K, resulting in a charge density wave (CDW) state. When a large enough magnetic field is applied the Zeeman energy will shift the transition temperature, T_{CDW} , of the CDW state following the equation,

$$\frac{\Delta T_{\text{CDW}}}{T_{\text{CDW}}(0)} = -\frac{\gamma}{4} \left(\frac{\mu_B B}{k T_{\text{CDW}}(0)} \right)^2$$

where B is the applied field, k is Boltzmann's constant, μ_B is the Bohr magneton and γ is a prefactor ~ 1 . Tiedje *et al.* first observed this phenomenon experimentally in TTF-TCNQ. The conductivity anisotropy (t_a : $t_c = 75:1:0.1$) and low transition temperatures ($T_{\text{CDW}} = 12$ K and 8 K for Au and Pt, respectively) make the $(\text{Per})_2\text{M}(\text{mnt})_2$ systems good candidates for exploring the effects of high fields on Q1D materials. The present work advances the findings of Bonfait and Matos, *et al.*, in studying this effect on $(\text{Per})_2\text{Pt}(\text{mnt})_2$ and $(\text{Per})_2\text{Au}(\text{mnt})_2$.

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Synthetic Metals, 153
 (2005) p. 361

SIMULTANEOUS MONITORING OF TOXIC METALS ON WHITE POPLAR (POPULUS) BY SWASV

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Leitão, Ruben A.E.¹; Silva, Hugo F.A.¹;
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Publicado em:
*Journal of Brazilian
Chemical Society, 16
(2005) p. 1275*

Square wave anodic stripping voltammetry (SWASV) was applied to the simultaneous determination of trace amounts of toxic metals Pb(II), Cd(II) and Cu(II) in white poplar (*populus*) leaves, used as bio-indicator and gathered in a chosen area of the city of Lisbon with very high traffic intensity. The leaves were dried and subsequently exposed to an acid digestion microwave process. Square wave parameters were optimized for the voltammetric analysis of the samples. The working electrode consisted of a thin mercury film (TMFE) deposited on the surface of vitreous carbon. The pair Ag/AgCl was used as the reference electrode and a Pt wire as the auxiliary electrode. Average concentrations (in mg of metal/kg of dry matter-leaves) of 2.6, 0.18, and 5.0 were obtained for Pb(II), Cd(II) and Cu(II), respectively. The value for lead coincides with the one obtained by the reference method based on Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS).

COMPARATIVE STUDY OF THE COPOLYMERIZATION KINETICS OF MONO AND DIVINYLBENZYL *p*-TERT-BUTYLCALIX[4]ARENE DERIVATIVES AND STYRENE

Costa, Alexandra I.; Barata, Patrícia D.; Prata, José V.

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A study of the copolymerization kinetics of 25,27-bis-(4-vinyl-benzyloxy)-26,28-dihydroxy-*p*-tert-butylcalix[4]arene (**1**) and 25,26,27-tripropoxy-28-(4-vinyl-benzyloxy)-*p*-tert-butylcalix[4]arene (**2**) with styrene (**St**) was undertaken. The radical copolymerizations were carried out in THF in the presence of benzoyl peroxide at 75°C for a certain period. Six molar feed ratios, ranging from 1:1 to 1:20 (**1** or **2** to **St**), were used to calculate the reactivity parameters. The copolymer composition was determined by FT-IR spectroscopy using a Beer's law plot obtained from the corresponding homopolymers. The reactivity ratio calculations were performed with the linearization methods of Fineman-Ross (F-R) and Kelen-Tüdös (K-T), assuming the validity of the so-called terminal model. In the copolymerization of the monoene **2**, similar reactivity ratios were found for the comonomers (*ca.* 1.2; K-T). On the other hand, the reactivity ratios calculated for the copolymerization of **1** with **St** yielded $r_{St} = 0.67$ and $r_{calix} = 3.0$ (K-T method). The higher reactivity of monomer **1** as compared to styrene is discussed in connection with our previously postulated cyclocopolymerization route.

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Supramolecular Chemistry, 2005
(in press; doi:
10.1080/10610270500450747).

RADICAL CYCLOPOLYMERIZATION OF A DIVINYLBENZYL-*p*-TERT-BUTYL-CALIX[4]ARENE DERIVATIVE

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Publicado em:

Reactive and Functional Polymers, 2005 (in press; doi: 10.1016/j.reactfunct-polym.2005.10.001)

The synthesis and characterization of a new homopolymer (poly **1**), obtained in the course of the radical polymerization of 25,27-bis-(4-vinyl-benzyloxy)-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene (**1**), is described. Homopolymerization of **1** in THF, using BPO or thermal initiation, afforded soluble polymers in good isolated yields (60-90%). Gel permeation chromatography (GPC) profiles showed unimodal distributions for all the analyzed polymers, which is indicative that chain branching reactions did not occur to a major extent. Molecular weights (M_n) ranging from 30000-60000 g mol^{-1} were reached within a 8h period, when the reactions were conducted at 0.06-0.5 mol% of BPO or thermally initiated, showing relatively narrow polydispersity indexes (1.5-2.0). The structure of the polymers was deduced upon analysis of their ^1H NMR and FT-IR spectra, which, in conjunction with GPC and solubility data led to their formulation as cyclopolymers.

LINEAR AND CROSSLINKED COPOLYMERS OF *p*-TERT-BUTYLCALIX[4]ARENE DERIVATIVES AND STYRENE: NEW SYNTHETIC APPROACHES TO POLYMER-BOUND CALIX[4]ARENES

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As an extension of our previous studies concerning the free radical copolymerisation of 25,26,27-tripropoxy-28-(4-vinyl-benzyloxy)-*p*-tert-butylcalix[4]arene (**3**) with styrylic monomers, we report herein on the synthesis and characterisation of new terpolymers derived from **3**, styrene and divinylbenzene, having nominal crosslinking degrees ranging from 4% to 40% wt. The terpolymers exhibited good thermal stabilities (DSC) and were prepared in good yields. Depending on the reaction conditions (dilution degree and aqueous phase to porogen ratio), materials with identical nominal crosslinking but otherwise differentiated morphologies and swelling abilities were obtained. In a related study, the radical polymerisation of styrene was carried out in the presence of a novel calix[4]arene derivative **4**, bearing two distal benzyl-vinyl groups in the lower rim. It is shown that, albeit the presence of two phenolic groups within the calixarene moiety, which could have functioned as inhibitors of the free radical polymerisation, the macrocycle was able to take part in the copolymerisation reaction, yielding new soluble and crosslinked polymers. In both cases, no pendant vinyl groups were found in the polymeric materials. The probable mechanisms underlying their formation are discussed.

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Functional Polymers,*
2005, 65, 9

SYNTHESIS, CHARACTERISATION AND CRYSTAL STRUCTURE OF THE BIMETALLIC CYANO BRIDGED $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)][\text{PF}_6]$

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The bimetallic cyano-bridged $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)][\text{PF}_6]$ (**1**) was prepared by reaction of $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuCl}]$ with *N,N'*-bis(cyanomethyl)ethylenediamine. The single crystal structure determined by X-ray diffraction showed crystallization on the triclinic *P1* space group with a perfect alignment of the cyanide bridges. This accentric crystallization was explored having in view the NLO properties at the macroscopic level, determined by the Kurtz Powder technique. Besides the very low efficiency values for the second harmonic generation, the value obtained for the bimetallic complex **1** showed to be higher than one of the parent complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuCN}]$ (**2**).

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Inorg. Chim. Acta.,
2005, 358, 2482-2488.

A SUPRAMOLECULAR ZIGZAG CHAIN OF ORGANOMETALLIC DIPOLES MEDIATED BY PF₆⁻ ANIONS

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The title compound (η^5 -cyclopentadienyl)(4-nitrobenzoni-trile-kN)(trimethylphosphine-kP)-iron(II) hexafluorophosphate, [Fe(C₅H₅)(C₇H₄N₂O₂)(C₁₈H₁₅O₃P)]PF₆, has been characterized by spectroscopic and X-ray diffraction in order to evaluate the tuning of the electron density at the metal centre and the extension of the π delocalization on the molecule due to the presence of phosphite and phosphine co-ligands. The compound crystallizes in the centrosymmetric space group $P2_1/c$, which destroys the possibility of exhibiting any quadratic non-linear optical properties. The packing shows a supramolecular zigzag chain of antiparallel cations connected via the PF₆⁻ anions through C-H...F ^{δ^-} interactions, with H...F distances ranging from 2.39 to 2.67 Å. Each zigzag chain is composed of isomeric organometallic fragments containing either *R* or *S* molecules. These chains are connected through weak intermolecular C-H...C interactions, forming a two-dimensional plane parallel to (101).

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Acta Crystallogr. C,
2005, C61, m386-
m389.

DENSITY FUNCTIONAL THEORY CALCULATIONS ON η^5 -MONOCYCLOPENTADIENYLCOBALT COMPLEXES CONCERNING THEIR SECOND-ORDER NONLINEAR OPTICAL PROPERTIES

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Density functional theory calculations were performed to determine first static hyperpolarizabilities (β) of model complexes $[\text{CoCp}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)(p\text{-NCC}_6\text{H}_4\text{R})]^{2+}$. The results show that these complexes have low hyperpolarizabilities which are due to weak electronic coupling between the organometallic fragment and the nitrile ligands. It was shown that in these complexes the electronic excitation responsible for second-order non-linear optical response is a ligand to metal charge transfer. The results also show the inverse relationship between the first hyperpolarizability and the corresponding electronic transfer energy gaps.

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J. Mol. Struct.:
THEOCHEM, 2005,
729, 109-113.

EMPIRICAL EXPRESSION OF PHOSPHORUS SOLUBILITY IN MOLTEN $\text{Fe}_{1-y}\text{Cr}_y$ GIVEN AS FUNCTIONS OF TEMPERATURE AND PHOSPHORUS ACTIVITY

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Chemical activity–temperature–composition (a – T – x – y) relationships determined by Knudsen effusion technique were made available for molten Fe–Cr–P system by a group of Russian researchers. Nevertheless, they were not presented in form of solubility x in $\text{Fe}_{1-y}\text{Cr}_y\text{P}_x$ as explicit functions of phosphorus activity a_P and temperature T for given y and thence they are not readily usable for evaluating P solubility in molten $\text{Fe}_{1-y}\text{Cr}_y$ at arbitrary T under certain a_P . In the present work, effort was invested to derive empirical expression for the solubility x in $\text{Fe}_{1-y}\text{Cr}_y\text{P}_x$ as functions of T and a_P at given y from the reported a_P – T – x – y relationships in discrete tabulated format. Such analytical expression of solubility x might allow us to proceed with more profound consideration for atomic interaction and atomic configuration in the molten $\text{Fe}_{1-y}\text{Cr}_y\text{P}_x$ on the basis of statistical thermodynamics.

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ISIJ International,
2005, 45, 1226–1231.

ALLENYLIDENE IRON(II) COMPLEXES AND THEIR DEPROTONATION, NUCLEOPHILIC ADDITION REACTIONS AND CATHODIC PROTONATION TOWARD ALKYNYL DERIVATIVES, A CHEMICAL AND ELECTROCHEMICAL STUDY

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Organometallics, 2005,
24, 4654-4665.

The allenylidene complexes *trans*-[FeBr(=C=C=CRR')(depe)₂][Y] (R = Me, R' = Ph **1**; R = R' = Ph **2**; R = R' = Et **3**; depe = Et₂PCH₂CH₂PtEt₂; Y = BF₄ or BPh₄) were obtained by reaction of *trans*-[FeBr₂(depe)₂] with the appropriate alkynol HC≡C-CRR'(OH), in MeOH and in the presence of Na[BF₄] or Na[BPh₄]. Deprotonation of **3** or nucleophilic γ -addition to **2** led to the neutral enynyl or alkynyl complexes *trans*-[FeBr{-C≡C-C(=CHMe)Et}(depe)₂] **4** or *trans*-[FeBr{-C≡C-CPh₂R''}(depe)₂] (R'' = CN **5a** or MeO **5b**), respectively. Complex **2** (Y = BPh₄) also leads to the cationic alkynyl compounds *trans*-[Fe(NCMe){-C≡C-CPh₂(X)}(depe)₂][BPh₄] (X = NMe₂ **6a** or NHMe **6b**) and *trans*-[Fe(NCMe){-C≡C-CPh₂(PMe₃)}(depe)₂Y₂ (Y₂ = [BPh₄]₂ **7a** or [BPh₄]_{2-x}Br_x **7b**), in acetonitrile solution, upon reaction with NHMe₂, NH₂Me or PMe₃, respectively. The complexes have been characterized by multinuclear NMR and IR spectroscopies, FAB-MS, elemental analysis and, in the cases of **5a** and **6a**, also by X-ray diffraction analysis.

Controlled potential electrolysis of **2** yields the alkynyl *trans*-[FeBr{-C≡C-CPh₂(H)}(depe)₂] **8** via a 2e⁻/H⁺ process, and the oxidation potential of the complexes, measured by cyclic voltammetry, has allowed to estimate the electrochemical Pickett P_L and Lever E_L ligand parameters for the cumulenic ligands. These are then ordered (together with related ligands) according to their net π -electron acceptor minus σ -donor ability as follows: carbynes > aminocarbyne > CO > vinylidenes > aryl allenylidene > alkyl allenylidene > NCR >> phosphonium alkynyl > cyanoalkynyl, Br, NCO⁻ > alkynyl, enynyl, aminoalkynyl.

SYNTHESES AND PROPERTIES OF Re(III) COMPLEXES DERIVED FROM HYDROTRIS (1-PYRAZOLYL)METHANES: MOLECULAR STRUCTURE OF [ReCl₂(HCp_z)₃](PPh₃)₂][BF₄]

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The complexes [ReCl₂{N₂C(O)Ph}(Hpz)(PPh₃)₂] **1** (Hpz = pyrazole), [ReCl₂{N₂C(O)Ph}(Hpz)₂(PPh₃)] **2**, [ReCl₂(HCp_z)₃](PPh₃)₂][BF₄] **3** and [ReCl₂(3,5-Me₂Hpz)₃(PPh₃)Cl] **4** were obtained by treatment of the chelate [ReCl₂{η²-N,O-N₂C(O)Ph}(PPh₃)₂] **o** with hydrotris(1-pyrazolyl)methane HCp_z (**1,3**), pyrazole Hpz (**1,2**), hydrotris(3,5-dimethyl-1-pyrazolyl)methane HC(3,5-Me₂pz)₃ (**4**) or dimethylpyrazole 3,5-Me₂Hpz (**4**). Rupture of a C(sp³)-N bond in HCp_z or HC(3,5-Me₂pz)₃, promoted by the Re centre, has occurred in the formation of **1** or **4**, respectively. All compounds have been characterized by elemental analyses, IR and NMR spectroscopy, FAB-MS spectrometry, cyclic voltammetry and, for **1**.CH₂Cl₂ and **3**, also by single crystal X-ray analysis. The electrochemical E₁ Lever parameter has been estimated, for the first time, for the HCp_z and the benzoyldiazenide NNC(O)Ph ligands.

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J. Organomet. Chem.,
2005, 690, 1947-1958.

SUPERCRITICAL CO₂ EXTRACTION OF γ -LINOLENIC ACID (GLA) FROM THE CYANOBACTERIUM ARTHROSPIRA (SPIRULINA) MAXIMA. EXPERIMENTS AND MODELING.

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147-152.*

The freeze-dried biomass of *Arthrospira* was submitted to supercritical CO₂ extraction, in a flow apparatus, at temperatures of 50 and 60 °C, pressures of 250 and 300 bar and flow-rates of 12.8, 19.6 and 29.5 g CO₂/min. The achieved extraction yields, using pure CO₂, were low and increased slightly with pressure and temperature and decreased with the flow rate.

In order to increase the extraction yield of the 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 CO₂.

A comparison between supercritical extraction and organic solvent extraction was also carried out, in what concerns lipid yields and fatty acid composition of total lipids.

Furthermore, a plug flow model, in which the resistance to internal mass transfer is considered to be the controlling step, was applied to the supercritical CO₂ extraction of lipids from the *Arthrospira maxima*.

INFLUENCE OF RARE EARTH ELEMENTS La, Nd AND Yb ON THE ACIDITY OF H-MCM-22 AND H-BETA ZEOLITES

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The influence of rare earth (RE) elements on the acidic properties of H-MCM-22 and H-Beta was studied by pyridine adsorption followed by infrared spectroscopy (FTIR) and n-heptane cracking, as a model reaction. The zeolites were submitted to ion exchange with rare earth nitrate solutions of La, Nd and Yb. The FTIR spectra of REH-MCM-22 indicate the presence of RE elements inside supercages and in the sinusoidal channels of the zeolite. After pyridine adsorption two additional bands are detected in REH-MCM-22 and REH-Beta, related to pyridine bonded to RE₃₊ cations.

The n-heptane cracking reaction shows that the effect of rare earth elements is related not only to the acidity but also with the porous structure of both zeolites. In H-Beta zeolite, the presence of RE elements enhances the acidity of the catalysts. In H-MCM-22 zeolite, the most relevant effect of rare earth elements is on the shape selectivity that becomes more pronounced with the ionic radius of the RE elements. The nature of the coke deposited on the two materials shows distinct profiles that are also related to its porous structure.

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Catalysis Today, 2005,
107-108, 663-670.

TOLUENE METHYLATION OVER PILLARED CLAYS WITH Al, Zr AND Al/Zr OXIDES

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Publicado em:
*Studies in Surface
Science and Catalysis,*
2005, 158B, 1469-
1476.

Pillared clays (PILCs), with Al, Zr and Al/Zr oxides, obtained from a natural montmorillonite from Benavila (Portugal), were investigated in terms of their structure (XRD), texture (N₂ and toluene adsorption), acidity (pyridine chemisorption) and catalytic performances on methylation of toluene. Zr content reflects on the doo1 values and on the acidity of PILCs, that present, besides Lewis sites, also Brönsted acid sites. All the solids showed activity to toluene alkylation revealing that, even the Brönsted acidic properties that proceed only from the clay sheets are enough to promote alkylation. A mixture of xylenes (XY) was obtained as the main reaction products, and the isomers distribution followed generally the order m ≥ o > p. Trimethylbenzenes (TMB) and ethyltoluenes (EtT) were also found, and on all the samples the selectivities were S_{XY} >> S_{TMB} > S_{EtT}.

ISOMERIZATION OF N-HEXANE ON BIFUNCTIONAL CATALYSTS Pt/HBEA AND Pt/HMCM-22 WITH RARE EARTH ELEMENTS

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The influence of rare earth (RE) elements La, Nd, and Yb was studied on the transformation of n-hexane using two catalysts with different porous structures, HBEA and HMCM-22. The zeolites were submitted to ion exchange with rare earth nitrate solutions of La, Nd and Yb, followed by platinum introduction. Platinum was characterized by Temperature Programmed Reduction (TPR-H₂) and by toluene hydrogenation. Pt/HBEA samples show higher hydrogenation activities than Pt/HMCM-22. In transformation of n-hexane both zeolites present high selectivity for the isomerization reaction. The presence of RE elements in Pt/HBEA increases the selectivity for di-branched isomers. Pt/HMCM-22 shows low selectivity in di-branched isomers due to shape selectivity effects provoked by the introduction of RE elements in the pores of this zeolite.

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Studies in Surface Science and Catalysis, 2005, 158B, 1875-1882.

AMIDASE ENCAPSULATED IN TTAB REVERSED MICELLES FOR THE STUDY OF TRANSAMIDATION REACTIONS.

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*Biocatalysis and
Biotransformation,*
2005, 23, 407-414.

Amidase, an amide hydrolase enzyme (E.C.3.5.1.4) with acyl transferase activity, was encapsulated in a reversed micellar system composed of cationic surfactant TTAB in heptane/octanol (80/20%) and phosphate buffer at w_0 11. The reaction used to study the effect of the reversed micellar system on the enzyme behaviour was a transamidation reaction. The effect of different parameters like surfactant concentration, buffer molarity and pH on the enzyme kinetics was evaluated. Both initial velocities and product yield were measured. The results indicated that high initial velocity of hydroxamic acid synthesis and also the highest yield (98%) were obtained using the lowest pH value. The effect of TTAB concentration was dependent on the buffer molarity used. The effect of the buffer molarity on the reversed micelles dimension was analysed by light scattering. These results showed that the buffer molarity had a strong influence on the reversed micelle radius that could be related with the enzyme activity.

APPLICATION OF FTIR SPECTROSCOPY FOR MONITORING HYDROLYSIS AND SYNTHESIS REACTIONS CATALYSED BY A RECOMBINANT AMIDASE.

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This study demonstrates the use of Fourier transform infrared (FTIR) spectroscopy for monitoring both synthesis and hydrolysis reactions catalyzed by a recombinant amidase (EC 3.5.1.4) from *Pseudomonas aeruginosa*. The kinetics of hydrolysis of acetamide, propionamide, butyramide, acrylamide, benzamide, phenylalaninamide, alaninamide, glycinamide, and leucinamide were determined. This revealed that very short-chain substrates displayed higher amidase activity than did branched side-chain or aromatic substrates. In addition, on reducing the polarity and increasing the substrates' bulkiness, a reduction of the amidase affinity for the substrates took place. Using FTIR spectroscopy it was possible to monitor and quantify the synthesis of several hydroxamic acid derivatives and ester hydrolysis products. These products may occur simultaneously in a reaction catalyzed by the amidase. The substrates used for the study of such reactions were ethyl acetate and glycine ethyl ester. Hydroxylamine was the nucleophile substrate used for the synthesis of acetohydroxamate compounds. Results presented in this article demonstrate the usefulness of FTIR spectroscopy as an important tool for understanding the enzyme structure–activity relationship because it provides a simple and rapid real-time assay for the detection and quantification of amidase hydrolysis and synthesis reactions in situ.

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Analytical Biochemistry, 2005, 346, 49-58.

CHARACTERIZATION OF MONOCLONAL ANTIBODIES AGAINST ALTERED (T₁₀₃I) AMIDASE FROM *Pseudomonas aeruginosa*

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*Molecular
Biotechnology, 2005,
30, 207-219.*

Monoclonal antibodies (MAbs) against mutant (T₁₀₃I) amidase from *Pseudomonas aeruginosa* were raised by hybridoma technology. To select MAbs suitable for immunoaffinity chromatography, hybridoma clones secreting polyol-responsive MAbs (PR-MAbs) were screened that bind antigen tightly but release under mild and nondenaturing elution conditions. It was found that about 10% of enzyme-linked immunosorbent assay (ELISA)-positive hybridoma produce these MAbs as their ag-ab complex can be disrupted by propylene glycol in the presence of a suitable salt. Two of these hybridoma clones (F6G7 and E2A6) secreting PR-MAbs against mutant amidase were selected for optimization of experimental conditions for elution of amidase by using ELISA elution assay. These hybridoma cell lines secreted MAbs of IgM class that were purified in a single step by gel filtration chromatography, which revealed a single protein band on native polyacrylamide gel electrophoresis (PAGE). Specificity studies of this MAB revealed that it recognized specifically a common epitope on mutant and wild-type amidases as determined by direct ELISA. This MAB exhibited a higher affinity for denatured forms of wild-type and mutant amidases than for native forms as revealed by affinity constants (K), suggesting that it recognizes a cryptic epitope on an amidase molecule. Furthermore, MAb E2A6 inhibited about 60% of wild-type amidase activity, whereas it activated about 60% of mutant amidase (T₁₀₃I) activity. The data presented in this work suggest that this MAB acts as a very useful probe to detect conformational changes in native and denatured amidases as well as to differentiate wild-type and mutant (T₁₀₃I) amidases.

A COMPARATIVE STUDY ON THE CORROSION RESISTANCE OF AA2024-T3 SUBSTRATES PRE-TREATED WITH DIFFERENT SILANE SOLUTIONS. COMPOSITION OF THE FILMS FORMED.

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This work reports a comparative study on the corrosion resistance of AA2024-T3 pre-treated with three different silane solutions. The silanes used for the pre-treatments of the AA2024-T3 panels were: 1,2-bis(triethoxysilyl) ethane (BTSE), bis- [triethoxysilylpropyl] tetrasulphide (BTESPT) and γ -mercapto propyl trimethoxysilane (MPS). The analytical characterisation of the silane films was performed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The corrosion performance of the pre-treated substrates was evaluated by electrochemical impedance spectroscopy (EIS). The results show that the pre-treatments based on silanes provide good corrosion protection of unpainted AA2024-T3. Painted substrates, previously pre-treated with the silane solutions also revealed improved corrosion resistance and good adhesion properties. Fatigue tests show that the silane pre-treatments do not affect the fatigue behaviour of the AA2024-T3. The work also discusses the formation of the protective silane films.

Publicado em:

Progress in Organic Coatings, 2005, Vol. 54, Nº 4, 322-331.

ANALYTICAL CHARACTERISATION AND CORROSION BEHAVIOUR OF BIS-[TRIETHOXSILYLPROPYL] TETRASULPHIDE PRE-TREATED AA2024-T3.

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2005, Vol. 47, Nº 3,
869-881.

This work aims at studying the corrosion behaviour of AA2024-T3 pre-treated with bis-[triethoxysilylpropyl]tetrasulphide. Simultaneously, the work investigates the influence of the Cu-rich intermetallic particles on the formation of the silane film. The analytical characterization of the silane films was performed by Auger electron spectroscopy and X-ray photoelectron spectroscopy. The corrosion performance of the pre-treated substrates was evaluated by electrochemical impedance spectroscopy. Atomic force microscopy associated with Kelvin probe was also used to determine the influence of the silane film on the Volta potential distribution on the alloy surface. The results show that copper present in the intermetallics plays an important role on the film formation.

ELECTRONIC STRUCTURE OF ANODIC OXIDE FILMS FORMED ON COBALT BY CYCLIC VOLTAMMETRY

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The chemical composition and degrees of oxidation of thin oxides films formed on cobalt by cyclic voltammetry have been investigated by Auger electron spectroscopy and XPS analysis. In addition the electronic properties of the films have been examined by capacitance measurements using the Mott-Schottky method and photoelectrochemistry. The analytical results show that the thickness of the cobalt oxide films increases with the number of cycles and varies from a few tens to a few hundreds of angströms. When observed by transmission electron microscopy and diffraction, the films appear compact and well crystallised (spinel structure). Capacitance measurements show that both very thin and relatively thick films exhibit p-type semiconductivity. The band structure model proposed and the interpretation of the oxidation processes in terms of lattice ionic defects, can explain the film growth mechanism. The study shows how the electric fields created by the development of space charges influence both ionic transport and electronic transfer of charges.

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October 2005).

EFFECT OF Cs IMPREGNATION ON THE PROPERTIES OF PLATINUM IN Pt/Na-BEA AND Pt/Cs-BEA CATALYSTS.

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The presence of alkali cations in zeolite framework provides peculiar basic properties that influence the characteristics and reactivity of supported metal particles. Particularly, the addition of increasing amounts of cesium in Pt/Na-BEA and Pt/Cs-BEA catalysts, by CsOH impregnation, leads to changes of the oxidation state and reducibility of Pt species present in the zeolite microporosity. For similar contents of impregnated Cs, the metal dispersion is higher in Pt/Cs-BEA than in Pt/Na-BEA series, showing that both the amount of Cs excess and the nature of the compensating cation affect the characteristics of the Pt species. In the case of Cs-overloaded Pt/Cs-BEA, the size of Pt nano-clusters is below 10 Å. The very small Pt nanoparticles in reduced Cs-overloaded Pt/Cs-BEA are particularly active in aromatization of n-hexane.

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107-108, 792-799.*

DERIVING ANALYTICAL SOLUBILITY FORMULAE FOR PHOSPHORUS IN MOLTEN Fe-Cr AS FUNCTIONS OF PHOSPHORUS ACTIVITY AND TEMPERATURE FROM DISCRETE SOLUBILITY DATA OBTAINED BY KNUDSEN EFFUSION TECHNIQUE

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Zaitsev *et al.* reported recently a set of equilibrium composition relationships for molten ternary Fe-Cr-P system as functions of temperature T and chemical activities, $a(\text{Fe})$, $a(\text{Cr})$ and $a(\text{P})$, of constituents, Fe, Cr and P, determined by Knudsen effusion technique. The data in their work were presented in conventional atomic fractions format for constituents, Fe, Cr and P, at specified values of $a(\text{Fe})$, $a(\text{Cr})$, $a(\text{P})$ and T . Such discrete presentation of equilibrium data is not readily usable by other researchers for desired evaluation of the solubility x of the single interstitial constituent P in this molten ternary system $\text{Fe}_{1-y}\text{Cr}_y\text{P}_x$ at arbitrary T under specified $a(\text{P})$ where y represents the atom fraction of Cr against the total atom fraction of Fe and Cr and x the atom fraction of P against the total atom fraction of Fe and Cr.

Thus, the effort was invested to convert the presented equilibrium data for the molten ternary Fe-Cr-P system by Zaitsev *et al.*¹ in form of atomic fractions into the $\text{Fe}_{1-y}\text{Cr}_y\text{P}_x$ format to represent explicitly the situation of partial occupation of interstitial sites by P in the substitutional $\text{Fe}_{1-y}\text{Cr}_y$ lattice. Then, analytical expressions for x as functions of T and $a(\text{P})$ were derived for respective y . At any given y , x was presented in form

$$x = Aa(\text{P})\exp(B\ln T - C/T)$$

and the values of the constants, A , B and C , were determined to yield the best least-mean-squares fit for the available equilibrium data presented by Zaitsev *et al.*. This expression was decided to be used as the empirical analytical expression for x with reference to the earlier publication.

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NEW HYDROTRIS(PYRAZOLYL)METHANE VANADIUM COMPLEXES

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Publicado em:
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6th Conference on
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Funchal, Portugal,
Março de 2005.*

In spite of the importance of complexes containing the tripodal ligands hydrotris(1-pyrazolyl)methane, and substituted ones, *e.g.*, in synthetic inorganic, bioinorganic and organometallic chemistries,¹ the coordination chemistry of these ligands at vanadium (III or IV) centres, and in contrast with the hydrotris(1-pyrazolyl)borate chemistry, has not yet been reported. The underdevelopment of this chemistry results from the difficulties associated with the synthesis of such ligands and the usually low yields.

In pursuit of our interest in the interaction of pyrazole-containing molecules with various metal ions, we have been studying the reactions of HCpz_3 (pz = pyrazolyl) and $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ or their isoelectronic tris(pyrazolyl)borates with Fe(II)^2 and Re(V)^3 sites, now we report the reactions of $[\text{VO}(\text{OEt})_3]$ and VCl_3 towards HCpz_3 or $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ leading to the coordination of the latter to the vanadium(III) or (V) centres. The syntheses and characterization of the new complexes by IR and multinuclear NMR spectroscopies, FAB-MS spectrometry, elemental analysis and electrochemical methods are reported. Further reactivity towards nitrogen unsaturated molecules, *e.g.*, cyanamides, nitriles, or phosphines is also discussed.

SYNTHESIS AND CHARACTERIZATION OF NOVEL IRON(II) AND RUTHENIUM(II) DIHYDROAZULENE COMPLEXES AS POTENTIAL PHOTOCHROMIC SWITCHES

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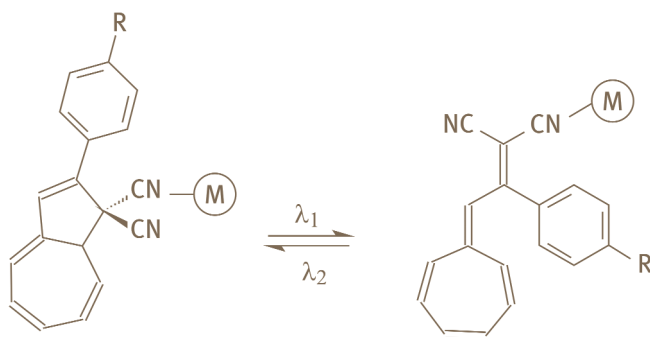
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During the last decade, light molecular switches have attracted much renewed attention due to their potential for applications to optical devices such as optical memories and switches. Although several organic photochromic molecules has been studied, photochromic systems involving transition metal complexes has been much less explored. Nevertheless, the role of the transition metal centres has found to be relevant in the intramolecular photosensitization of the photochromic process. The present communication reports our results on the synthesis and functionalisation of dihydroazulene type molecules, known as light molecular switches. The coordination of these chromophores to fragments $[M(\eta^5-C_5H_5)(dppe)]^+$ ($M=Fe(II), Ru(II)$) and $[Fe(\eta^5-C_5H_5)(CO)_2]^+$ through nitrile or acetylide group, lead to a new family of compounds. The new complexes were characterised by the usual spectroscopic IR, 1H and ^{13}C NMR techniques. Studies by UV/Vis spectroscopy were performed in order to characterise the photochromic behaviour of the new complexes.

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R = $C_6H_4NO_2$, $C_6H_4C\equiv C$, $C_6H_4C\equiv C-M$

M = $[Fe(\eta^5-C_5H_5)(dppe)]^+$, $[Ru(\eta^5-C_5H_5)(dppe)]^+$, $[Fe(\eta^5-C_5H_5)(CO)_2]^+$

SYNTHESIS AND CHARACTERIZATION OF NOVEL OCTAHEDRAL [FeCl(DMPE)₂(NCR)][PF₆] COMPOUNDS

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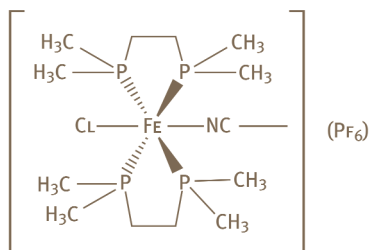
Materials with nonlinear optical (NLO) properties have many potential applications in photonic devices. Organometallic chemistry has emerged as a promising area of research to obtain new materials with enhanced NLO properties due to the large hyperpolarizabilities, fast response times and architectural flexibility of organometallic compounds.

Our studies with phosphinecyclopentadienyliron(II) or ruthenium(II) fragments containing *p*-substituted benzonitriles lead to new compounds with significant NLO properties. In the search of new systems, we synthesised iron(II) octahedral complexes with the general formula [FeX(biphosphine)₂(NCR)](PF₆) (X=Cl, I or H; biphosphine=DMPE, DPPE, dppen, odppb; NCR=mono- or dinitrobenzonitriles) with interesting results towards NLO properties.

In this communication, we report the synthesis and characterization of a series of [FeCl(DMPE)₂(NCR)](PF₆) derivatives. The acceptor capacity of the nitrile chromophore was changed with the coordination of one or two nitro groups and, also, with the change, both in length and structure, of the conjugated backbone. The new compounds were characterized by usual spectroscopic techniques and the X-Ray diffraction structure of compound [FeCl(DMPE)₂(2,4-NCC₆H₃(NO₂)₂)](PF₆) is presented. The results were analysed to evaluate the electronic richness of the metal centre and the influence of the structural changes of the coordinated nitrile, which may give some contribution to understand the relationships between structure and NLO responses. Density functional theory calculations were also performed to access the first static hyperpolarizabilities (β) of these compounds using the GAMESS-US program package and appropriate basis sets to ensure calculations accuracy.

Publicado em:

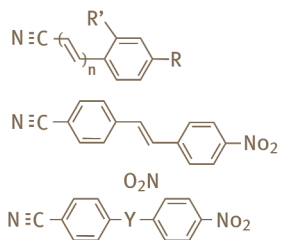
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$R = \text{NO}_2, \text{N}(\text{CH}_3)_2$; $R' = \text{H}$; $n = 0, 1$

$R = R' = \text{NO}_2$; $n = 0$

$Y = (E)\text{-CH=CH}$; CC ; CH=N-NH



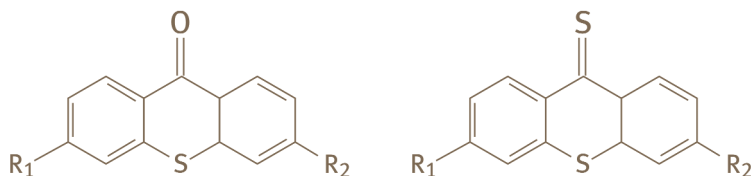
SÍNTESE E CARACTERIZAÇÃO DE COMPLEXOS DERIVADOS DE η^5 -MONOCICLOPEN-TADIENILO DE FERRO(II) E RUTÊNIO(II) COM LIGANDOS TIOXANTENOS SUBSTITUÍDOS: MATERIAIS PROMISSORES PARA NLO?

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Publicado em:
*Livro de Abstracts da
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A intensa actividade de investigação nos materiais moleculares com propriedades de Óptica Não Linear (NLO) tem produzido uma grande variedade de novos cromóforos. Entre eles, os complexos metálicos representam uma classe de materiais crescente e emergente. Na procura de novos sistemas com potenciais propriedades de NLO, temos desenvolvido trabalho na síntese e caracterização de unidades orgânicas fotocromicas, baseadas em alcenos estereoimpedidos e respectiva coordenação a fragmentos organometálicos de ferro (II) e de rutênio (II). O interesse destes compostos consiste na introdução de cromóforos espaçadores com estruturas potencialmente helicoidais, o que permite a determinação das contribuições dipolares eléctrica e magnética para as propriedades de NLO, com grande interesse na área dos materiais fotorefractivos. O presente trabalho descreve a síntese e caracterização de unidades orgânicas derivadas do esqueleto tioxanteno (uma das unidades constituintes dos alcenos estereoimpedidos) e sua posterior coordenação aos fragmentos $[\text{CpM}(\text{dppe})]^+$ ($\text{M}=\text{Fe}(\text{II}), \text{Ru}(\text{II})$).



$\text{R}_1 = \text{NC-[M]}, \text{CC-[M]}$; $[\text{M}] = [(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Fe}], [(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}]$; $\text{R}_2 = \text{NO}_2$

Estes novos complexos foram caracterizados pelas técnicas espectroscópicas usuais de I.V., ^1H e ^{13}C RMN. Os dados são analisados com o objectivo de avaliar os efeitos da coordenação no esqueleto π deslocalizado do cromóforo. Estudos de UV/Visível foram igualmente efectuados, uma vez que a existência de bandas de transferência de carga é, em geral, um indicador da existência de propriedades de NLO.

SYNTHESIS OF NEW PERMETHYLCYCLOPENTADIENYL Ru(II) DERIVED COMPLEXES FOR NONLINEAR OPTICS

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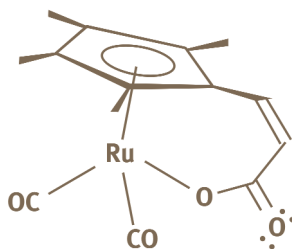
The increasing interest in the preparation of new chromophores suitable for electro-optical properties has initiated a search for the synthesis of new molecules based on highly polarized, organic, inorganic and organometallic molecules. One general common structural feature found for organic and organometallic molecules has been the existence of a backbone consisting of an electron-donating group connected to an electron-accepting group by a conjugated π -bridge.

Our strategy on design of organometallic molecules in view of materials possessing non-linear optical properties (NLO) has been based on systems where the chromophore is placed in the plane containing the metal center, being the charge transfer originated by π back-donation $d\pi-\pi^*$ ligand. In these structures the organometallic moiety playing the role of donating group is based on $\eta^5-C_5H_5M(LL)$ with $M = Ru(II)$ and $Fe(II)$.

In the present communication we report a new approach on the design of molecules for NLO, based on a hemi-helical structure formed through a permethylcyclopentadienyl ligand possessing a functionality on the pendant arm.

The aim of our work is to use different functional groups on the pendant arm to coordinate at the metal center leading to a formation of hemi-helical structures.

The new compounds were synthesized by Wittig reactions of $Ru(LL)(\eta^5-C_5(CH_3)_4CHO)$ with the adequate phosphonium salts of the pretended pendant arm, and characterized by the usual spectroscopic data, namely 1H , ^{13}C , ^{31}P and IR, and by elemental analysis. Studies on the UV-Vis spectra will be presented in order to understand existence of electronic transfer and solvatochromism.



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NONLINEAR OPTICAL PROPERTIES OF η^5 -MONOCYCLOPENTADIENYLIRON COMPLEXES FROM DFT CALCULATIONS

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Recently, organometallic complexes have emerged as potential building blocks for second-order nonlinear optical (SONLO) materials in view of their potential application in the area of integrated optics. Unlike organic molecules, whose optical nonlinearities have been extensively studied by computational methodologies using both semi-empirical and ab initio methods, organometallic systems have received much less attention due to the difficulty in the calculation of reliable hyperpolarizabilities in the presence of transition metal atoms. ZINDO has been the most widely used program to calculate SONLO coefficients of organometallic compounds. A more reliable approach, using the density functional theory (DFT) method is less explored but has been increased in the recent years.

Experimental work on η^5 -monocyclopentadienyliron complexes with *p*-nitro benzonitrile ligands showed that the first hyperpolarizability decreases with increasing conjugation length of the chromophores. EHMO calculations performed on model complexes $[\text{FeCp}(\text{PH}_3)_2(\textit{p}\text{-NCR})]^+$ confirms this behavior and showed that the larger values of experimental hyperpolarizabilities correspond to lower HOMO-LUMO gaps. For similar complexes possessing a thiophene based conjugated backbone, a dramatic increase in experimental first hyperpolarizability with increasing conjugation length was observed. The explanation of this different behaviour was not definitively established. In order to get a better understanding on the electronic factors that may be responsible for the SONLO behavior of these compounds and their correlation with experimental spectroscopic and electrochemical data, high accuracy DFT calculations using GAMESS-US were made in model complexes $[\text{FeCp}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)(\text{NC}\{\text{SC}_4\text{H}_2\}_n\text{NO}_2)]^+$ ($n=1-3$). Spatial localization of electron charge as been performed to gain insight into the nature of the chromophores binding to the metal center. First static hyperpolarizability was calculated, compared with experimental results and correlated to the HOMO-LUMO gaps.

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A NEW METALLODENDRIMER FAMILY USING RUTHENIUM COMPLEXES AS BUILDING BLOCKS

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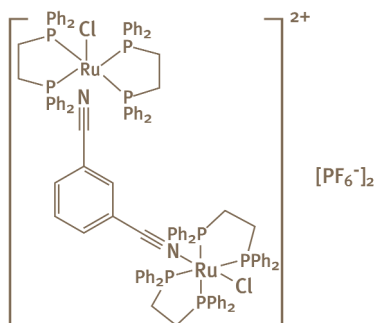
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Metallodendrimers are of great interest because of their many excellent properties, potential applications and attractive advantages over their polymeric counterparts in that they possess a precise molecular architecture as well as a predetermined chemical composition. We started to synthesise a metallodendrimer family[2] based on two types of core molecules: 1,3-dicyanobenzene (DCB) and 1,3,5-tris(4-ethynylbenzo-nitrile)benzene (TBEBN, an acceptor with an extended π -system and octopolar symmetry). The organic fragments are bonded by ruthenium complex fragments, of general formula $Ru(PP)_2$ ($PP = (PMe_3)_2, dpmm, dppe$) inserted at specific nodes and having organometallic fragments carefully chosen by their significant values of quadratic and cubic hyperpolarizabilities, arranged at the periphery of the dendritic structure.

Best results were obtained in the reactions with *cis*- $RuCl_2(dppe)_2$, for example $[1,3-(trans-RuCl(dppe)_2(NC)_2C_6H_4)]_2[PF_6]_2$ (Figure 1) is formed as the only product with the DCB, as a central core. In the case of *trans*- $RuCl_2(dpmm)_2$, a mixture of the appropriate *cis*- and *trans*-complex were obtained in a ratio of 9:1, while with *trans*- $RuCl_2(PMe_3)_4$ the required main product is accompanied by the formation of an undesired binuclear complex, $[Ru(PMe_3)_3]_2[\mu-Cl]_3[PF_6]$ (~12%). The metallodendrimers grows in a stepwise manner, prepared by a divergent synthetic methodology, from the central core to the periphery. Full characterization and electrochemical studies will also be presented.



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Março de 2005.

NEW LIGANDS FOR THE PREPARATION OF RUTHENIUM BASED MOLECULAR WIRES

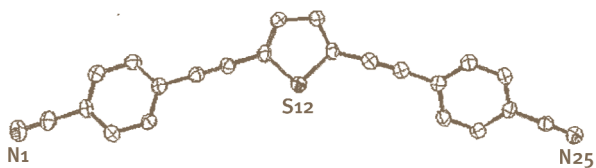
Vertlib, V.¹; Mesquita, J.C.¹; Rodrigues, J.¹;
Robalo, M. Paula^{2,3}; Nättinen, K.⁴; Rissanen, K.⁴

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One of the current interests of our research group is the chemistry of supramolecular ruthenium complexes with electronic and optical properties having in view their application as nanoelectronic components. Among the possible nanoelectronic components, molecular wires are indispensable elements of future molecular-scale electronic devices, and their fabrication has been one of the central issues in nanochemistry. One of our research goals is the preparation and study of the ruthenium based molecular wires. As a matter of fact, the use of highly conjugated bridging organic ligands is crucial for the efficient electronic transfer between the ruthenium metal centres.

Two new conjugated bridging ligands have been prepared by Pd-catalysed cross coupling reactions - 2,5-bis-(4-trimethylsilylethynylphenyl)-thiophene and 2,5-bis-(4-cyanophenylethynyl)-thiophene. All ligands have been prepared and completely characterized by means of NMR (¹H, ¹³C{¹H}), FTIR and EI MS spectroscopy. The electrochemical behaviour was studied by cyclic voltammetry. 2,5-bis-(4-cyanophenylethynyl)-thiophene has also been characterized by single crystal X-ray structural analysis (Figure 1). The compound belongs to the monoclinic space group P2₁/n, $a = 5.4557(11) \text{ \AA}$, $b = 19.467(4) \text{ \AA}$, $c = 15.592(3) \text{ \AA}$, $V = 1655.1(6) \text{ \AA}^3$, $Z = 4$, $D_c = 1.342 \text{ g cm}^{-3}$, $\mu = 0.201$, $R = 10.56$, $wR = 0.1066$. There are some distortions from a perfectly planar geometry in the structure. The phenyl ring at the N25-end is in 36° angle with respect to the plane of the thiophene. The angle between the two arms is 145.4°. The packing of the molecules is dictated by weak intermolecular interactions between the N1, N25, S12 and the aromatic hydrogens. There are also some weak $\pi \dots \pi$ interactions between the phenyls and the nitriles.



Molecular Structure of 2,5-bis-(4-cyanophenylethynyl)-thiophene.

The synthesis and the characterization of molecular wires of type Type III architectures (M-Bridge-M), the most important type of molecular wires architectures, containing e. g. $[\text{RuCl}(\text{dppe})_2]$ fragments and these new ligands are under way.

NEW CYANO-BRIDGED RUTHENIUM COMPLEXES FOR NON-LINEAR OPTICS

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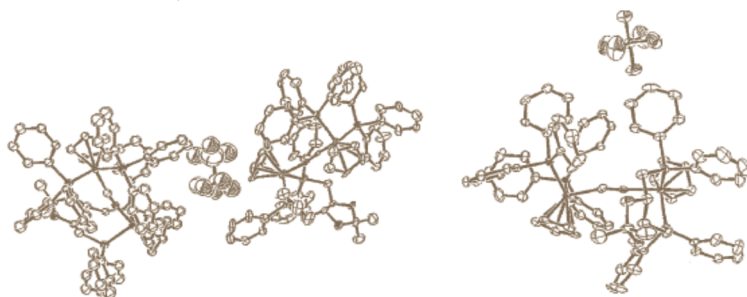
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Publicado em:
*Livro de Abstracts da
6th Conference on
Inorganic Chemistry,
Funchal, Portugal,
Março de 2005.*

Organometallic compounds are quite new objects for non-linear optics. One of the most common approaches on the design of both mono and binuclear compounds with NLO properties has been based on the charge transfer in donor- π -system-acceptor structures which are, in the case of binuclear compounds, metallic containing fragments. Although only few reports have been published so far using the cyanide anion as a bridge between metal fragments, the reported values foresee promising NLO properties for this type of structures. The effectiveness of the electronic transfer through the $-\text{C}\equiv\text{N}-$ bridging group was explored by binding the $[(\text{NH}_3)_5\text{RuIII}]$ acceptor moiety to several donor ruthenium fragments such as $\text{Ru}^{\text{II}}(\text{CN})_5$, $\text{Ru}^{\text{II}}\eta^5\text{-Cp}(\text{PPh}_3)_2$ or $\text{Ru}^{\text{II}}\eta^5\text{-Indenyl}(\text{PPh}_3)_2$. The reported significant β values for these compounds as well as a previous NLO value reported by our team have prompted us to synthesise the cyano-bridged complexes $[\text{CpRu}(\text{PPh}_3)_2\text{CNRu}(+\text{DIOP})\text{Cp}](\text{OTf})$ (**1**) and $[\text{CpRu}(\text{PPh}_3)_2\text{CNRu}(+\text{DIOP})\text{Cp}](\text{PF}_6)$ (**2**). Both compounds crystallized in noncentrosymmetric triclinic spatial groups – $P2_1$ in the case of (**1**) and $C2$ in the case of (**2**), that allowed us to expect the existence of NLO properties. Compounds (**1**) and (**2**) are completely characterized by means of NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$), IR and ESI MS TOF spectroscopical methods. The electrochemical behaviour of the prepared compounds was studied by cyclic voltammetry.



Molecular structure of compounds (**1**) (left) and (**2**) (right).

NON-LINEAR OPTICAL PROPERTIES OF IRON NITRILE COMPLEXES WITH PSEUDO-OCTAHEDRAL COORDINATION

Wenseleers, W.¹; Campo, J.¹; Teixeira, A.P.S.^{2,3};
Robalo, M. Paula^{2,4}; Garcia, M.H.^{2,5};
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Organometallic complexes with large molecular hyperpolarisabilities are studied using hyper-Rayleigh scattering measurements. By means of a nitrile linkage, an organometallic donor group is incorporated in the plane of a conjugated, acceptor substituted ligand to form an efficient push-pull system. As we demonstrated previously, ruthenium and especially iron cyclopentadienyl complexes can act as unusually effective donor groups. A pseudo-octahedral coordination, achieved with two phosphine ligands, results in an even more electron-rich organometallic group yielding very large hyperpolarisabilities, combined with more synthetic versatility. Design strategies for obtaining favorable crystal structures with perfectly aligned chromophores are also discussed.

Publicado em:

Livro de Abstracts da International Conference on Organic Photonics and Electronics 2005 (ICOPE2005) & 8th International Conference on Organic Nonlinear Optics (ICONO'8), Tohoku, Japan, Março de 2005.

MOLECULAR FIRST HYPERPOLARIZABILITIES OF PSEUDO-OCTAHEDRALLY COORDINATED HYDRIDENITRILEIRON(II) COMPLEXES DETERMINED WITH HYPER-RAYLEIGH SCATTERING

Campo, J.; Wenseleers, W.; Goovaerts, E.; Robalo, M. Paula^{2,3}; Teixeira, A.P.S.^{2,4}; Garcia, M.H.^{3,5}; Dias, A.R.²

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Livro de Abstracts da European Conference on Nonlinear Optical Spectroscopy (ECONOS 05), Oxford, UK, Abril de 2005.

Organometallic materials are very interesting towards nonlinear optics (NLO) and are preferable to the inorganic counterparts because of their large first hyperpolarizabilities β , fast response times and architectural flexibility. Inspired by the promising results obtained with our previous study of η^5 -monocyclopentadienyl compounds, additional improvements of the metallic donor group and the acceptor substituted conjugated

ligand are now introduced in order to further optimize the NLO response combined with other molecular properties. NMR and IR spectroscopic data, confirming a strengthening of the metallic electron donor group, have indeed been obtained. In particular, the enhancement is realized by replacing the η^5 -monocyclopentadienyl ring by a second bidentate phosphine ligand (dppe: 1,2 bis(diphenylphosphino)ethane), the acceptor is strengthened by the introduction of an extra nitro group at the ortho position of the last phenyl ring of the conjugated backbone and the nitrile ligand itself is optimized by variation in both length and structure. The improved complexes have a pseudo-octahedral coordination on the transition metal, yielding more possibilities for fine-tuning the molecular structure. An extra ligand can now be bound to the metal *trans* to the conjugated ligand, serving as a 'spacer group' to avoid anti-parallel alignment of the dipolar chromophores and thus obtaining a noncentrosymmetric arrangement, as needed for second-order NLO. The near resonant molecular β values of this new series of hydridenitriliron complexes are evaluated by means of the hyper-Rayleigh scattering (HRS) technique, using a setup based on an optical parametrical amplifier pumped by a Ti:sapphire regenerative amplifier and with nanosecond gated parallel detection of a small spectral area around the second harmonic. The high values obtained (up to 1130×10^{-30} esu) are interpreted in terms of the two-level model and are correlated with spectroscopic data.

THE BEHAVIOUR OF HYDROTRIS(PYRAZOLYL)METHANES AND LITHIUM TRIS(PYRAZO-LYL)METHANESULFONATES AT RHENIUM CENTRES

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The current growth of interest in the coordination chemistry of N₃ tripodal neutral tris(1-pyrazolyl)alkanes and the novel class of more hydrophilic anionic ligands tris(pyrazolyl)methanesulfonates, is related to their applications in catalysis and synthetic inorganic, bioinorganic and organometallic chemistries.¹

In pursuit of our interest in the coordination and/or activation of nitrogen unsaturated molecules by transition metal centres we report the reactions of HCpz₃ (pz = pyrazolyl), HC(3,5-Me₂pz)₃, Li[SO₃Cpz₃] and Li[SO₃C(3,5-Me₂pz)₃] towards rhenium(V) and (IV) centres such as [ReCl₂{η²-N,O-N₂C(O)Ph}(PPh₃)₂],² [ReOCl₃(PPh₃)₂], [ReCl₃(NCMe)-(PPh₃)₂] and [ReCl₄(NCMe)₂]. The syntheses and characterization of the new complexes by IR and multinuclear NMR spectroscopies, FAB-MS spectrometry and elemental analysis are reported. Further reactivity towards other nitrogen or carbon unsaturated molecules is also discussed.

Publicado em:

Livro de Abstracts da 20th International Conference on Coordination and Bioinorganic Chemistry, Smolenice, Eslováquia, Junho de 2005

ELECTROCHEMICAL BEHAVIOUR OF PYRAZOLE, HYDROTRIS (PYRAZOLYL)METHANE AND TRIS(PYRAZOLYL)METHANESULFONATE RHENIUM COMPLEXES

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Publicado em:
Livro de Abstracts do VIII Encontro Ibérico de Electroquímica e XIII Encontro da Sociedade Portuguesa de Electroquímica, Covilhã, Portugal, Julho de 2005

The current growth of interest in the coordination chemistry of tris(1-pyrazolyl)methanes and the derived tris(1-pyrazolyl)methanesulfonates, is related to their applications in catalysis and synthetic inorganic, bioinorganic and organometallic chemistries.¹

In pursuit of our interest in the coordination and/or activation of nitrogen unsaturated molecules by transition metal centres we have studied the reactions of HCpz₃ (pz = pyrazolyl), HC(3,5-Me₂pz)₃, Li[SO₃Cpz₃] and Li[SO₃C(3,5-Me₂pz)₃] towards rhenium(V), (IV) and (III) centres, leading to the pyrazole (Hpz) complexes² [ReCl₂{N₂C(O)Ph}(Hpz)(PPh₃)₂], [ReCl₂{N₂C(O)Ph}(Hpz)₂(PPh₃)], [ReClF{N₂C(O)Ph}(Hpz)₂(PPh₃)], [ReCl(NCMe)(Hpz)₂], [ReCl₂(3,5-Me₂Hpz)₃(PPh₃)] [Cl], the hydrotris(pyrazolyl)methane complexes [ReCl₃(HCpz₃)], [ReCl₂(HCpz₃)PPh₃] [BF₄] and the tris(1-pyrazolyl)methanesulfonate compounds [ReOCl₂(SO₃Cpz₃)] and [ReO₃(SO₃Cpz₃)].

The electrochemical behaviour of the above complexes and their parent ones, as studied by cyclic voltammetry and controlled potential electrolysis, in aprotic media, at a Pt electrode, is now reported.

In addition, the Lever E_L ligand parameter for the tris(1-pyrazolyl)methanesulfonate ligand is for the first time estimated by using the reported³ S_M and I_M values for the Re^{III/IV} redox couple, the known ligand E_L values for the monodentate ligands and $E^{\text{red}}_{1/2}$ values of our compounds. The obtained electrochemical results are discussed in terms of electron richness of the Re centres and the electronic properties of the ligands.

ELECTROCHEMICAL BEHAVIOUR OF TRIS(PYRAZOLYL)METHANE AND TRIS(PYRAZO-LYL)METHANESULFONATE VANADIUM COMPLEXES

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In spite of their relevance in synthetic inorganic, bioinorganic and organometallic chemistries,¹ vanadium complexes containing the N₃ tripodal ligands hydrotris(1-pyrazolyl)methane, and substituted ones, have not yet been the object of an electrochemical investigation.

We now report the results of our study of the electrochemical behaviour of new vanadium complexes,² obtained by reaction of VO(OEt)₃ and VCl₃ towards HCpz₃, HC(3,5-Me₂pz)₃, Li[SO₃Cpz₃] and Li[SO₃C(3,5-Me₂pz)₃], carried out in 0.2 M [Bu₄N][BF₄]/CH₂Cl₂, by cyclic voltammetry (CV) at a Pt-disc electrode and by controlled potential electrolysis (CPE) at a Pt-gauze electrode.

Such behaviours are discussed in terms of electron richness of the V centres and the electronic properties of the ligands.

Publicado em:

Livro de Abstracts do VIII Encontro Ibérico de Electroquímica e XIII Encontro da Sociedade Portuguesa de Electroquímica, Covilhã, Portugal, Julho de 2005

CONVERSION OF ETHANE INTO ACETIC ACID CATALYSED BY TRIS(PYRAZOLYL)-METHANE Re COMPLEXES

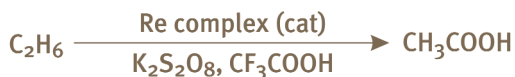
Martins, L.M.D.R.S.^{1,2}; Pombeiro, A.J.L.²;
Alegria, E.C.B.^{1,2}; Espada, A.A.¹

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13th IUPAC
International
Symposium on
Organometallic
Chemistry Directed
Towards Organic
Synthesis, Geneve,
Suíça, Julho de 2005.*

Transition-metal-catalysed functionalization of alkanes is one of the most challenging fields of organometallic chemistry. In particular, the achievement of metal catalysed selective oxidation of lower alkanes such as ethane, to higher value chemicals is of great practical interest. Despite that, Re-catalysed alkane oxidations are very little explored.¹ Herein we report the catalytic oxidation of ethane to acetic acid under mild conditions by rhenium(III) complexes with tris(pyrazolyl)methane or pyrazole ligands² in the presence of the peroxodisulfate salt $K_2S_2O_8$ as the oxidizing agent and in trifluoroacetic acid as the solvent:



Reaction conditions, turnover numbers and yields are reported.

NEW IRON(II) AND RUTHENIUM(II) COMPLEXES WITH STERICALLY OVERCROWDED ALKENES: SYNTHESIS AND CHARACTERISATION

Jacob, C.¹; Robalo, M. Paula^{1,2}; Garcia, M.H.^{1,3}; Piedade, M.F.M. da^{1,3}; Duarte, M.T.¹; Dias, A.R.¹

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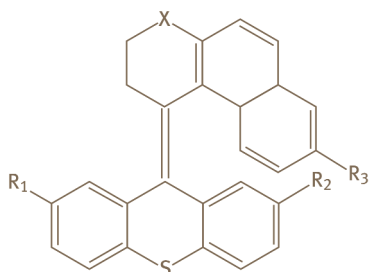
² Departamento de Engenharia Química, ISEL, Lisboa, Portugal

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The search for new organometallic complexes with high values of hyperpolarisabilities β has been an area of interest during the last twenty years, due to their potential technological applications in telecommunication and computer industries.

The introduction of helically shaped systems, such as sterically overcrowded alkenes, allows the presence of measurable dipolar and magnetic contributions to NLO effects, which is an area of interest for photorefractive materials. The helical environment in these systems is based on the presence of bulky substituents that cause sufficient hindrance between the upper and lower half of the alkene and enforce a helical distortion in the entire molecule.

We report herein the synthesis and characterisation of organic overcrowded alkenes based in two building blocks, the thioxanthene and phenanthrene units, for which synthetic pathways were developed, and the coordination of these ligands to iron(II) and ruthenium(II) fragments, such as $[\text{CpM}(\text{dppe})]^+$ and $[\text{M}(\text{dppe})_2(\text{H})]^+$ ($\text{M} = \text{Fe}(\text{II}), \text{Ru}(\text{II})$).



X = S, CH₂;
 R₁ = NC[M], CC[M];
 [M] = [Fe(η^5 -C₅H₅)(dppe)], [Ru(η^5 -C₅H₅)(dppe)],
 [Fe(dppe)₂(H)];
 R₂ = NO₂; R₃ = H, CH₃

The new complexes were characterised by the usual spectroscopic UV-Vis, IR and NMR techniques and for some intermediates X-ray diffraction studies were also performed. Structural characterisation and properties will be discussed.

Publicado em:

Livro de Abstracts da XVth FECEM Conference on Organometallic Chemistry, Budapeste, Hungria, Setembro de 2005.

NEW TRIS(PYRAZOLYL)METHANE RHENIUM AND VANADIUM COMPLEXES: SYNTHESIS AND CATALYTIC APPLICATION IN ALKANE OXIDATION

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Publicado em:
*Livro de Abstracts da
 5th International
 School of
 Organometallic
 Chemistry, Camerino,
 Itália, Setembro de
 2005.*

The chemistry of tris(pyrazolyl)methane transition metal complexes is attracting a high interest in particular due to the discovery of their application in catalysis and synthetic organometallic chemistry. Nevertheless, the coordination chemistry of tris(pyrazolyl)methanes at rhenium and vanadium sites still remains an underdeveloped field [1]. Herein we report the synthesis of new rhenium and vanadium complexes with the N₃ tripodal neutral ligand hydrotris(1-pyrazolyl)methane (HCp₃; pz = pyrazolyl) or its derived disubstituted hydrotris(3,5-dimethyl-1-pyrazolyl)methane [HC(3,5-Me₂pz)₃], *e.g.*, [ReCl₃{HC(3,5-R₂pz)₃}] (R = H or Me) or [VO(HCp₃)](BF₄)₃, respectively. In some cases we have observed the conversion of the tris(pyrazolyl)methane into the corresponding pyrazole, as *e.g.*, in [ReCl₃(NCMe)(Hpz)₂]. The complexes have been characterized by IR and multinuclear NMR spectroscopies, FAB-MS spectrometry and elemental analysis.

We also report the study of the catalytic behaviour of these rhenium and vanadium complexes in the peroxidative oxidation of alkanes to the corresponding alcohols and ketones. Turnover numbers and yields are indicated.

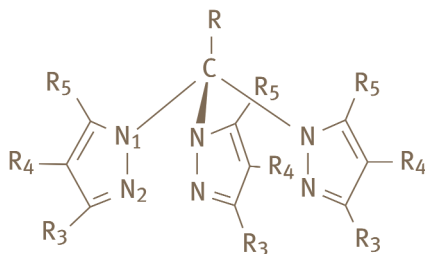
MICROWAVE-ASSISTED SYNTHESIS OF TRIS(PYRAZOLYL)METHANES, AN IMPROVED PREPARATIVE METHOD

Martins, L.M.D.R.S.^{1,2}; Espada, A.A.¹;
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Tris(pyrazolyl)methanes (TPM), with three N-deprotonated pyrazole rings (pz) bound to a carbon atom, constitute a potentially very important class of tripodal nitrogen-donating ligands in modern coordination chemistry.



TPM

Despite the fact that hydrotris(pyrazolyl)methane, $\text{HC}(\text{pz})_3$ ($\text{R}=\text{R}_3=\text{R}_4=\text{R}_5=\text{H}$), was first reported in 1937¹, until recently the chemistry of tris(pyrazolyl)methanes has been relatively underdeveloped, mainly due to their inconvenient multi-step syntheses which result in very low yields. In fact, even the most improved method² requires a reflux for three days, the separation of products from the reaction mixtures is tedious and difficult (*e.g.*, column chromatography or fractional sublimation), and the yields are still low (*e.g.*, 24% for HCpz_3).

Herein we report a convenient microwave-assisted synthesis of tris(pyrazolyl)methanes which, by taking advantage of this alternative and efficient source of energy, greatly shortens the reaction times (from days to a few hours) and leads to an improved product yields. The effects of reaction conditions (*e.g.*, temperature and pressure) are also indicated.

Publicado em:

Livro de Abstracts da 9th International Chemical Engineering Conference, Coimbra, Portugal, Setembro de 2005.

SYNTHESIS OF NEW HYDROTRIS(1-PYRAZOLYL)METHANE AND TRIS(1-PYRAZOLYL)METHANESULFONATE COMPLEXES IN AQUEOUS MEDIUM

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Publicado em:
*Livro de Abstracts da
Green Chemistry: a
Solution for the World,
Almeria, Espanha,
Dezembro de 2005.*

The coordination chemistry of tris(1-pyrazolyl)methanes is a field of a current growing interest under various viewpoints, not only for improving a fundamental knowledge (e.g., on structural and physico-chemical properties and on reactivity) but also to develop topics with an applied character such as catalysis. In fact, the anionic derivatives tris(1-pyrazolyl)methanesulfonates, which are hydrolytically stable and soluble in polar protic solvents, are particularly promising for liquid biphasic catalysis in view of the water-solubility of their transition metal complexes. However, the coordination chemistry of these N₃ tripodal ligands has been reported only scarcely [1].

Here we report the synthesis and characterization, including the crystal structure and electrochemical behaviour, of new pyrazole (Hpz), hydrotris(1-pyrazolyl)methane (HCpz₃) and tris(1-pyrazolyl)methanesulfonate (SO₃Cpz₃)⁻ complexes of Re(III, V and VII) [2] (e.g., [ReCl₂{N₂C(O)Ph}(Hpz)(PPh₃)₂], [ReCl(X){N₂C(O)Ph}(Hpz)₂(PPh₃)] (X = Cl or F), [ReCl₂(3,5-Me₂Hpz)₃(PPh₃)]Cl, [ReCl₃{HC(3,5-R₂pz)₃}] (R = H or Me) [ReCl₂(HCpz₃)(PPh₃)] [BF₄], [ReOCl(SO₃Cpz₃)(PPh₃)]Cl and [ReO₃(SO₃Cpz₃)], Fe(II) (e.g., [FeCl₂(HCpz₃)] and V(IV and V) (e.g., [VO{HC(3,5-R₂pz)₃}] [BF₄]₃ (R = H or Me), [VCl₃(SO₃Cpz₃)] and [VCl₂(SO₃Cpz₃)(L)]Cl (L = DMF or η²-HC≡CCH₂CH₂OH)).

The above complexes can act as catalysts in the oxidation of ethane to acetic acid or in the peroxidative oxidation of cyclohexane to cyclohexanone and cyclohexanol, under mild conditions (at room temperature) in aqueous medium, as examples with industrial significance within the challenging field of alkane functionalization.

PEROXIDATIVE OXIDATION OF CYCLOHEXANE IN AQUEOUS MEDIUM BY RHENIUM AND IRON COMPLEXES

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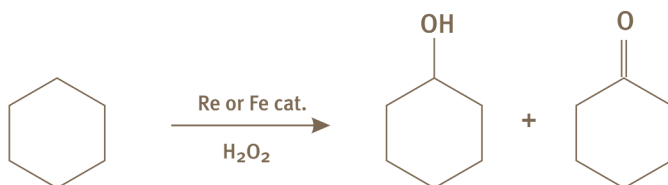
The oxidation of cyclohexane is an important industrial process, since some of its products such as cyclohexanone and adipic acid are used as intermediates for Nylon manufacture. Previous studies have revealed that the main products obtained upon oxidation of cyclohexane are cyclohexanone, cyclohexanol and adipic acid. [1]

A current process used in industry consists in the use of homogeneous cobalt salts, using dioxygen as oxidant at 150 °C. This process gives cyclohexanone (85 % selectivity) with an yield of ca. 4 %. [2] Hydrogen peroxide is a convenient oxidant since it just produces water as a by-product, but the conversions and turnovers of the cyclohexane oxidation with H₂O₂ are usually still low.

The new hydrotris(pyrazolyl)methane and tris(pyrazolyl) methanesulfonate complexes [ReCl₃(HCpz₃)] and [ReO₃(SO₃Cpz₃)], as well as related pyrazole and parent complexes, such as [ReClF{N₂C(O) Ph}(Hpz)₂(PPh₃)] and [ReOCl₃(PPh₃)₂], act as catalysts in the peroxidative oxidation of cyclohexane to cyclohexanone and cyclohexanol, under mild conditions (at room temperature and using an aqueous solution of H₂O₂), with TONs over 200.

The hydrotris(pyrazolyl)methane, tris(pyrazolyl)methanesulfonate and hydrotris(pyrazolyl)borate iron(II and III) were also tested in this catalytic process.

The effects of various parameters such as the amount of catalyst, type of oxidant or of solvent, presence of a radical trap, time, oxidant-to-catalyst molar ratio and temperature are reported.



A comparison with the activity of other Re [3] and Fe [4] catalysts reported by us will also be provided.

Publicado em:

Livro de Abstracts da Green Chemistry: a Solution for the World, Almeria, Espanha, Dezembro de 2005.

NEW TRIS(PYRAZOLYL)METHANE VANADIUM COMPLEXES: SYNTHESIS AND CATALYTIC ACTIVITY

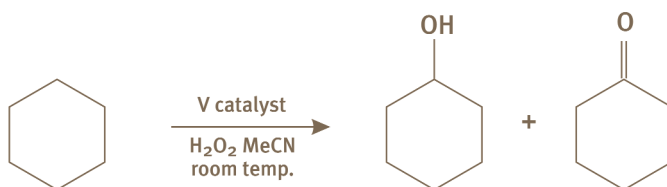
Silva, T.F.S.^{1,2,3}; Martins, L.M.D.R.S.^{1,2}; Pombeiro, A.J.L.²

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Although some vanadium compounds can display interesting catalytic properties, their application in catalysis is still an underdeveloped field of research. The conversion of alkanes into oxygenated derivatives (namely of cyclohexane into cyclohexanol and cyclohexanone, Scheme 1) has been extensively studied [1] in view of the high industrial significance of such products.

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Scheme 1

Moreover, the chemistry of tris(pyrazolyl)methane transition metal complexes is currently attracting a high interest in particular due to the discovery of their application in catalysis and synthetic organometallic chemistry. Nevertheless, the coordination chemistry of tris(pyrazolyl)methanes at vanadium sites still remains very little explored [2].

Herein we report the synthesis of new vanadium(IV) complexes with the N₃ tripodal anionic tris(1-pyrazolyl)methanesulfonate SO₃Cpz₃⁻ (pz = pyrazolyl) ligand, which are water-soluble and can act as catalysts in the peroxidative oxidation of cyclohexane to cyclohexanone and cyclohexanol, by H₂O₂, under mild conditions in aqueous medium.

The new complexes have been characterized by IR and multinuclear NMR or EPR spectroscopies, FAB-MS spectrometry and elemental analysis. For the catalytic studies the turnover numbers and yields are indicated.

AVALIAÇÃO DO POTENCIAL METANÓGENICO DE RESÍDUOS ORGÂNICOS

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Na Europa, cerca de 50% do total dos resíduos sólidos urbanos, contendo *ca.* 30% de fracção orgânica, excluindo o papel e o cartão, são ainda colocados em aterro sanitário (Mata-Alvarez *et al.*, 2000).

Uma das soluções apontadas para o tratamento de resíduos orgânicos biodegradáveis é a digestão anaeróbia. Este processo de tratamento origina genericamente dois sub-produtos: o designado composto orgânico, resíduo da digestão, cuja estabilidade composicional permite a sua aplicação a solos com deficiência em matéria orgânica e o biogás, cuja valorização energética pode ser significativa.

Em Portugal, a legislação comunitária (Directiva 1999/31/CE) tem sido transposta por forma a promover a redução da quantidade de resíduos enviados para aterro, nomeadamente a referida fracção orgânica. No entanto, o limitado número de aplicações de digestão anaeróbia para os resíduos sólidos urbanos actualmente existentes evidencia a necessidade de se proceder a estudos aprofundados nesta área, que se coadunem com o tipo de resíduos sólidos produzidos em Portugal e com a diversidade das condições específicas existentes, nomeadamente sistemas de recolha, armazenamento e pré-tratamento.

No presente estudo pretendeu-se avaliar o potencial metanogénico de diversos substratos com vista à futura aplicação da digestão anaeróbia a resíduos sólidos orgânicos (RSO) em larga escala. Os RSO estudados compreenderam resíduos, compostos maioritariamente por vegetais e frutas, obtidos por separação manual dos resíduos produzidos no Mercado Abastecedor da Região de Lisboa - MARL, e relva, bem como diversas misturas dos referidos resíduos (Tabela 1).

Tabela 1 – Composição das misturas utilizadas nos testes de potencial metanogénico

Mistura	M1	M2	M3	M4	M5
Vegetais e frutas	100%	-	50%	25%	75%
Relva -	100%	50%	75%	25%	

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A caracterização dos substratos foi efectuada através da determinação do teor de sólidos totais e voláteis, de pH, de matéria orgânica (CQO) e de azoto.

Os ensaios de potencial metanogénico foram realizados em condições mesófilas, tendo por base o método de Owen *et al.* (1979), utilizando reactores com 1 L de capacidade.

A quantificação do biogás produzido foi determinada volumetricamente e a sua caracterização obtida por GC.

Da avaliação dos resultados obtidos para o potencial metanogénico das misturas utilizadas (M1 – M5), constatou-se que as misturas contendo 100% de relva (M2) e 75% de relva (M4) conduziram aos valores mais elevados de metano produzido (Figura 1).

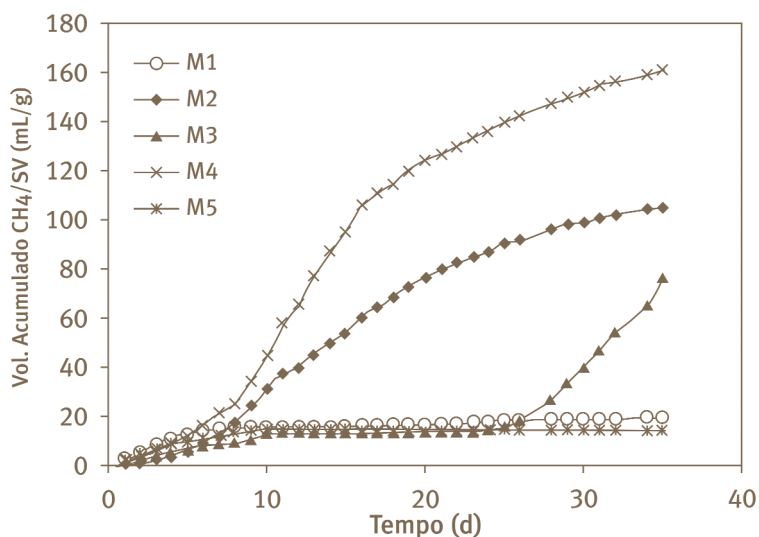


Figura 1 – Produção de metano para as misturas M1 a M5.

Os resultados obtidos serão analisados de igual modo relativamente a outros parâmetros de controlo, designadamente, o teor de ácidos orgânicos voláteis presentes em cada mistura ao longo do ensaio.

COPOLYMERISATION KINETICS OF A DIVINYL *p*-TERT-BUTYLCALIX[4]ARENE DERIVATIVE AND STYRENE DETERMINED BY FT-IR SPECTROSCOPY

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In recent years, a growing interest as emerged in the field of polymeric materials containing calixarenes, regarding their potential usefulness as chemical sensor devices (Blanda and Adou, 1998; Yilmaz *et al.*, 1999). Calixarenes are a well-known class of synthetic receptor macrocyclic molecules, and its synthesis and applications were comprehensively reviewed (Asfari *et al.*, 2001).

Our previous work in this area showed the ability of a monovinylcalixarene derivative, 25,26,27- tripropoxy-28-(4-vinyl-benzyloxy)-*p*-tert-butylcalix[4]arene, to be copolymerised with styrene (St), using the suspension polymerisation technique, with conversions up to 60% after 24h of reaction (Barata *et al.*, 2004). It was found, from the ¹H NMR integrals corresponding to the former monomers, that the composition of the copolymers thus prepared showed a good correlation with the feeding ratios, which was interpreted as a result of the similar reactivity of the monomers involved.

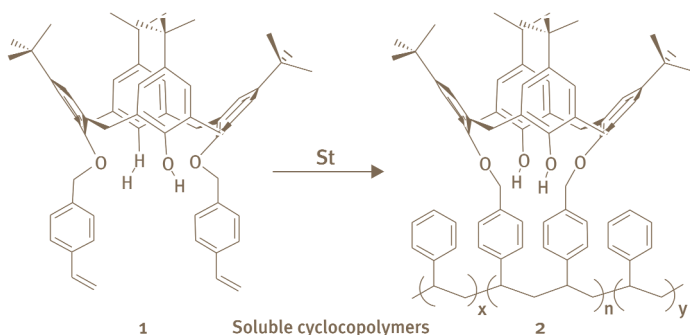
The tethering of two benzyl-vinyl units to the calix[4]arene core was then envisioned with the aim of render the monomer the ability to function as a brancher, a crosslinker agent, or even linearly cyclo-copolymerise. Thus, when the radical polymerisation of styrene was carried out in the presence of the new bifunctional calix[4]arene monomer **1**, bearing two distal vinyl polymerisable groups in the lower rim, new soluble and crosslinked polymeric materials were obtained (Mendes *et al.*, 2005). The presence of two unprotected phenolic subunits in the macrocycle structure, which could have been deleterious given the known inhibitory effects of this functionality to the radical polymerisation, didn't preclude the outcome of the reaction. One of the routes postulated to account for the results was the cyclocopolymerisation, involving an intramolecular addition between the two vinylic units followed by an intermolecular step either with another calixarene molecule or with styrene. When, under suspension polymerisation at 82°C using toluene as porogen and acacia powder as stabiliser, a molar feed ratio of calixarene **1** to St of 1:20 was used, a soluble copolymer was obtained in 31% yield with a molar composition of *ca.* 1:13 (1:St). This result clearly pointed to a fairly higher

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reactivity of the comonomer **1** as compared to styrene.

To gain further information about the reactivity of the monomers in the free-radical polymerisation, a study of the copolymerisation kinetics of 25,27-bis-(4-vinyl-benzyloxy)-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene (**1**) with styrene was undertaken. The radical copolymerisations were carried out in THF in the presence of benzoyl peroxide at 75°C for a certain period of time. Copolymers were isolated by precipitation in methanol, after solvent evaporation and dissolution of the residue in a minimum amount of dichlorometane. This operation was repeated until the copolymer was freed from unreacted calixarene, as evaluated by TLC control of the samples. The reaction time for each copolymerisation was set between 1.5h to 2.5h in order to keep the conversions under 10% wt (gravimetrically determined) to minimise the compositional drift that would probably occur during the reactions. Six molar feed ratios, ranging from 1:1 to 1:20 (**1** to St), were used to calculate the reactivity parameters. The copolymer composition was determined by transmission FT-IR spectroscopy against a calibration curve obtained from the correspondent homopolymers, using the ratio of the areas of the bands peaking at 818 cm⁻¹ (homocalix) and 699 cm⁻¹ (homoSt). The best fit equation generated through linear least squares analysis was $y=0.5216x+0.1569$ ($R^2=0.9924$), where x represent the actual molar polymer ratio (0 to 20; homoSt:homocalix) and y is the ratio of the areas (homoSt:homocalix) referred above. The reactivity ratio calculations were performed with the linearisation methods of Fineman-Ross (FR) and Kelen-Tüdös (KT), assuming the validity of the so-called terminal model. The two methods yielded similar values for the reactivity ratios: $r_{St}=0.71$ (FR) and 0.67 (KT) and $r_{calix}=3.38$ (FR) and 2.98 (KT). These values mean that the rate of adding a calixarene unit to a growing chain is always higher, as compared to the styrene addition, irrespective of the nature of the terminal radical. The high reactivity of monomer **1** in radical polymerisations is in accordance with our previously postulated cyclopolymerization route.



A NEW CLASS OF CYCLOPOLYMERS DERIVED FROM DIVINYLBENZYL -*p*-TERT-BUTYLCALIX[4]ARENE

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Synthetic helical structures are of great interest in terms of their characteristic features and potential widespread applications such as those related with molecular recognition (chemical sensors, catalysis and separation processes) and molecular scaffolding. Single-handed helical polymers may be obtained either through the so-called helix-sense-selective polymerization or through macromolecular helicity induction. In the former case a chiral factor is provided during the polymerization step (homochiral monomer, catalyst or initiator) while in the later the helicity is generated from the interaction of an optically inactive polymer with an external homochiral source. Acid-base and host-guest interactions have been reported in this context. Cyclopolymerization of bifunctional monomers is a useful method for obtaining polymers with well-organized structures. The use of a calix[4]arene unit possessing distal 4-vinylbenzyl groups at its lower rim was thought as a convenient rigid monomer to perform the task of selective ring-closing, yielding a cyclopolymer with constrained conformational mobility, which, hopefully, will show molecular helicity induction capabilities.

Here we report on the synthesis and characterization of a new cyclopolymer (poly $\mathbf{1}$), obtained in the course of the radical homopolymerization of 25,27-bis-(4-vinyl-benzyloxy)-26,28-dihydroxy-*p*-tert-butylcalix[4]arene ($\mathbf{1}$). Polymerization of $\mathbf{1}$ in THF, using BPO or thermal initiation, afforded soluble polymers in good isolated yields (60-90%). Gel permeation chromatography profiles of all the analyzed polymers showed unimodal distributions, which is indicative that chain branching reactions did not occur at a major extent. Molecular weights (M_n) ranging from 30000-60000 molg⁻¹ were reached within a 8h period, when the reactions were conducted at 0.06-0.5 mol% of BPO or thermally initiated, showing relatively narrow polydispersity indexes (1.5-2.0). The structure of the polymers was deduced upon analysis of their ¹HNMR and FT-IR spectra.

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COMPARATIVE STUDY OF THE COPOLYMERIZATION KINETICS OF MONO AND DIVINYLBENZYL *p*-TERT-BUTYLCALIX[4]ARENE DERIVATIVES AND STYRENE

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Our previous work showed the ability of 25,26,27-tripropoxy-28-(4-vinyl-benzyloxy)-*p*-*tert*-butylcalix[4]arene **1** to be copolymerized with styrene (St), using a suspension polymerization technique. Good correlation was found between the composition of the copolymers and the feeding ratios, which was interpreted as a result of the similar reactivity of the monomers involved. When styrene was polymerized in the presence of the bifunctional calix[4]arene monomer **2**, 25,27-bis-(4-vinyl-benzyloxy)-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene, bearing two distal vinylbenzyl polymerizable groups in the lower rim, soluble and crosslinked polymers were obtained, depending on reaction conditions. In the later case, however, the rate of incorporation of **2** in the final polymer was apparently much higher than for styrene, resulting in molar compositions (1:13; 2:St) that were different from the initial feed (1:20; 2:St). In the present communication we present the results of the copolymerization kinetics of mono and divinylbenzyl derivatives of *p*-*tert*-butylcalix[4]arene with styrene. The radical copolymerisations were carried out in THF in the presence of benzoyl peroxide at 75°C. The copolymer compositions were determined by transmission FT-IR spectroscopy and the reactivity ratios calculated with the linearization methods of Fineman-Ross (FR) and Kelen-Tüdös (KT), assuming the validity of the so-called terminal model. In the copolymerization of the monoene **1**, similar reactivity ratios were found for the comonomers (*ca.* 1.2). On the other hand, the reactivity ratios calculated for the copolymerization of **2** with St, yielded $r_{St}=0.71$ (FR) and $r_{calix}=3.38$ (FR). The high reactivity shown by the calixarene **2** in radical polymerizations will be discussed in connection with our previously postulated cyclocopolymerization route.

INFLUÊNCIA DA PRESENÇA DE LANTÂNIO NOS CATALISADORES Pt/HMOR, Pt/HMCM-22 E Pt/HBEA NA REACÇÃO DE HIDROISOMERIZAÇÃO DE n-HEXANO

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Estudou-se a influência de pequenas quantidades de lantânio (La) em catalisadores bi-funcionais de estruturas distintas, Pt/HMOR, Pt/HMCM-22 e Pt/HBEA. Na hidroisomerização do n-hexano observou-se que a presença de La aumenta a selectividade em produtos bi-ramificados apenas na estrutura HBEA. O efeito dos catiões La³⁺, de dimensão considerável, nas outras estruturas conduz à diminuição da selectividade em DMBs, e a um simultâneo aumento dos produtos de cracking.

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e Materiais Porosos
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Portugal, Maio de
2005.*

HYDROISOMERIZATION OF n-HEXANE ON PLATINUM HMOR, HMCM-22 AND HBEA DOPED WITH LANTHANUM

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Setembro de 2005.*

The effect of La introduction in the isomerization of n-hexane was studied in zeolites with three different structures, HMOR, HMCM-22 and HBEA. The introduction of La and Pt was performed by ion exchange. The textural characterization of the samples by N₂ adsorption showed a decrease in V_{microp.} upon the introduction of La for HMOR and HMCM-22 structures, indicating the existence of space limitations inside the pores of these zeolites.

In isomerization of n-hexane the presence of La increases the selectivity into di- branched isomers for Pt/HBEA. In the other two structures, Pt/HMOR and Pt/HMCM-22 a decrease in di-branched products is observed, caused by space limitations in the unidimensional pore structure of Pt/HMOR and in the narrow 10-membered ring pores and apertures of Pt/HMCM-22. This decrease of selectivity is due to the cracking of reaction intermediates that occurs preferentially on these two zeolites.

ESTUDOS DE REACTIVIDADE EM MISTURAS METANOL-FORMAMIDA E ACETONITRILO-FORMAMIDA. CORRELAÇÃO COM PROPRIEDADES DAS MISTURAS

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É reconhecido o papel fundamental que os solventes desempenham nos sistemas químicos. Para além dos solventes puros, as misturas de solventes são igualmente uma fonte importante de informação sobre os processos em solução, pelo facto de constituírem sistemas mais complexos, devido ao acréscimo de possíveis interacções entre os vários constituintes da própria mistura.

Na sequência de estudos anteriores com misturas de solventes próticos e apróticos, neste trabalho foram determinadas as constantes de velocidade, k , a 25.00 °C, relativas à heterólise do 2-bromo-2-metilpropano, num total de 17 fracções molares das misturas binárias MeOH/Formamida e MeCN/Formamida, utilizando uma técnica condutimétrica. Para as mesmas misturas foram determinados experimentalmente os índices de refacção e as bandas UV-Vis de absorção características de uma série de indicadores solvatocrómicos. Estes valores experimentais permitiram determinar vários parâmetros descritores das misturas.

Uma metodologia envolvendo análises de correlação entre as constantes de velocidade e os descritores de solvente, permitiu a identificação das principais interacções soluto-solvente-solvente que influenciam o processo reaccional.

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REACTIVITY STUDIES OF 2-BROMO-2-METHYLPROPANE IN BINARY AND TERNARY MIXTURES OF PROTIC AND APROTIC SOLVENTS. CORRELATIONS WITH SOLVENT STRUCTURE

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 Organic Reactivity,
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 2005.*

Solvents play a major role in many chemical processes, influencing solubility and partition, chemical equilibria, spectroscopy, electrochemistry and reaction rates. Along with pure solvents, mixtures of solvents have been increasingly studied and applied in life sciences, industrial processes and environmental protection. The study of solvent mixtures is considerably more complex, due to the various possible interactions between different mixture components and, in reactive studies, also between substrates and distinct solvent molecules. Nevertheless, mixtures are potentially more informative, since the variability of most of their properties can be significantly increased through adequate choice of components and compositions. Following the work on the structural characterization of binary and ternary mixtures of protic and aprotic solvents, it was our aim this time to enlarge the matrix of solvents used so that a reliable application of multivariate data analysis can be performed.

In this work, we report rate constants, k , for the reaction of 2-bromo-2-methylpropane in the binary mixtures MeOH/1-PrOH, MeOH/MeCN and 1-PrOH/MeCN and in the ternary mixture MeOH/1-PrOH/MeCN, in a total of 73 molar fractions. A conductimetric technique, using an automated conductance bridge was employed, in order to obtain the solvolytic rate constants in the various mixtures ($[t\text{-BuBr}] = 10^{-3} \text{ mol dm}^{-3}$). At least three experiments were performed for each system. The study was performed at 25.00 °C with a temperature control always better than ± 0.01 °C.

A correlation analysis between rate constants and solvent descriptors previously determined was applied. This procedure allowed the identification of the major solute-solvent-solvent interactions influencing the rate processes.

MODELLING PREFERENTIAL SOLVATION IN TERNARY SOLVENT MIXTURES

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Solvents mixtures represent still today a challenge in chemistry. The complexity of the phenomena that can occur in these systems increases, due to the formation of new or different solute-solvent-solvent interactions. Preferential solvation is one of these phenomena, and results from the solute's different degree of interaction with the distinct components of the solvent mixture. This leads to a solvent composition in the proximity of the solute molecules (cybotatic region) different from that of the solvent "bulk", which may affect several solvent properties, including reactivity. This behaviour has been studied by several experimental techniques from which the most extensively used is the UV-Vis analysis of the solvatochromic dependence of several dyes. Preferential solvation has been explained by several theoretical models, as for instance, the competitive preferential solvation model, the "quasi-lattice quasi-chemical" theory and the Kirkwood-Buff integrals formalism. Following the work on the structural characterization of binary and ternary mixtures of protic and aprotic solvents, the absence of models capable of describing solvatochromism of ternary mixtures emerged, namely for the Reichardt betaine(30), or the associated normalized Dimroth-Reichardt polarity parameter (E_T^N). A model with the capacity to describe the ternary but also the binary mixtures and beside the properties prediction capabilities could provide also insight to the solution process.

In this work, we developed an extension to ternary systems of the preferential solvation model for binary mixtures, first proposed by Skwierzynski and Connors and later expanded by Rosés et al. The deduction of this model for preferential solvation in ternary mixtures lead to the following expression, , where for a component i , Y_i represents the value of the property Y , x_i^0 its the molar fraction in the bulk, f_{ij} the preferential solvation number of component j relative to component i and m the number of solvating molecules.

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$$Y = \frac{Y_1(x_1^0)^m + Y_2 f_{2/1}(x_2^0)^m + Y_3 f_{3/1}(x_3^0)^{\frac{m}{2}} + Y_{12} f_{12/1}(x_1^0 x_2^0)^{\frac{m}{2}} + Y_{13} f_{13/1}(x_1^0 x_3^0)^{\frac{m}{2}} + Y_{23} f_{23/1}(x_2^0 x_3^0)^{\frac{m}{2}} + Y_{123} f_{123/1}(x_1^0 x_2^0 x_3^0)^{\frac{m}{3}}}{(x_1^0)^m + f_{2/1}(x_2^0)^m + f_{3/1}(x_3^0)^m + f_{12/1}(x_1^0 x_2^0)^{\frac{m}{2}} + f_{13/1}(x_1^0 x_3^0)^{\frac{m}{2}} + f_{23/1}(x_2^0 x_3^0)^{\frac{m}{2}} + f_{123/1}(x_1^0 x_2^0 x_3^0)^{\frac{m}{3}}}$$

In order to test the proposed model, we have applied it with success to the mixture already studied by us (MeOH/1-ProH/MeCN) and to one other ternary system (MeOH/EtOH/Acetone) with published values.

RECENT ADVANCES IN CORRELATION ANALYSES OF TERTIARY ALKYL HALIDES HETEROLYSIS REACTIONS.

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The heterolysis reactions of tertiary alkyl halides, being very sensitive to solvent changes, represent an interesting class of reactions to probe solvent and solvation effects. There are numerous modifications that can be introduced either in these substrates' leaving groups and/or in their carbonated skeleton which can be used to provide some insight into the nature of the solute-solvent interactions associated with these processes.

Multiparametric linear regression (MLR) analyses have been used to correlate various solvent properties with the logarithm of rate constants, $\log(k)$ (or the Gibbs energy of activation, $\Delta^\ddagger G$) leading to the calculation of several regression coefficients that are measures of the substrate's sensitivity to those properties. One of the most used multiparametric equations has been the TAKA equation.²⁻⁴

Our research group has endeavoured⁴⁻⁷ on a project to test TAKA's applicability to a vast number of structurally different substrates pursuing, among other objectives, a deeper comprehension of the role of each property on these reaction processes.

The 260 $\log(k)$ values (10 substrates in 26 solvents) presented in this communication will provide experimental evidence for: *i*) the need of including an extra solvent property besides those considered in the original TAKA equation; *ii*) the importance of the nucleophilicity descriptor (based on an unambiguous definition of the underlying concept⁸) and the relation of its coefficient value to the carbonated skeleton structure, and *iii*) the dependence of the electrophilicity coefficient value solely from the substrate's leaving group chemical features. The work now presented also explores the rationale behind the attained results. Finally, it strongly suggests as well the need for additional studies specifically designed to further understand the role of solvent's structuredness and viscosity in reactivity.

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COMPARATIVE STUDIES OF SOLVENT EFFECTS IN THE HETEROLYSES OF TERTIARY ALKYL HALIDES: GRUNWALD-WINSTEIN PLOTS VS. ENLARGED TAKA EQUATION.

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 Roma, 2005.*

Grunwald-Winstein (G-W) plots were initially developed to quantify solvent's ionizing power in a given solvolysis reaction.¹ Later, Bentley *et al.*² assembled a multiparametric equation claimed to quantify also solvent's nucleophilicity. In both cases, model reactions³ were used to build up scales for these properties.

TAKA equation⁴ has also been extensively used to evaluate solvent's involvement in solvolyses.^{5,7} Recently we have extended this equation with the inclusion of a further solvent descriptor which improves its interpretative ability.⁸ Unlike the G-W approach, solvent descriptor values used by the TAKA equation are attained outside a reactivity context. Often, researchers using these two different approaches disagree in their conclusions, a fact that has been referred to be responsible for creating the impression that it is pointless to further pursue these mechanistic elucidation studies. This is probably due, among other aspects, to a widespread confusion over the concept of nucleophilic assistance.⁹ With this in mind, it seemed thus interesting to perform a confrontation between results provided by those two lines of investigation in order to disclose the real differences and similarities between them.

The work now presented reveals unsuspected affinities between these two analyses regarding the solvent's participation in reactivity. Both surveys show the importance of the solvent's nucleophilicity/basicity in the reactivity of less constrained tertiary alkyl halides (*t*-Bu's) and that this importance diminishes with the increase of the carbonated skeleton around the tertiary carbon. By analogy with the behaviour of the corresponding adamantyl compounds, it is also possible to distinguish differences between chlorides and iodides solvation modes, being the latter more influenced by the solvent's dipolarity and less by its electrophilicity.

Finally, we have drawn attention to some relevant statistical aspects and to the fact that the enlarged TAKA equation (or even its original version) is more discriminative and therefore more informative than G-W plots.

DETERMINAÇÃO DO TEOR EM SÓDIO E POTÁSSIO EM MEL MONOFLORAL

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O conhecimento da composição mineral é um indicador importante da qualidade dos produtos alimentares. Os elementos metálicos presentes nos alimentos podem ocorrer naturalmente ou resultar de processos de fabrico e armazenamento e deverão ser rigorosamente identificados e quantificados em virtude dos efeitos que podem causar na saúde pública.

Em continuação do programa experimental que tem vindo a ser desenvolvido nos Laboratórios de Controlo Analítico do ISEL, o qual se tem centrado na pesquisa de elementos metálicos em alimentos, o presente trabalho tem como principal objectivo o doseamento do sódio e do potássio em mel produzido em Portugal.

A análise foi efectuada através de espectrometria de absorção atómica, utilizando uma chama de ar-acetileno. O método foi optimizado em termos de intensidade da fonte emissora, caudal de acetileno e altura de queimador. Na preparação das soluções foi utilizado cloreto de cézio de modo a prevenir a ionização dos elementos a dosear. Após caracterização fisicoquímica, as amostras de mel com diferente origem floral foram reduzidas a cinzas e analisadas nas condições experimentais seleccionadas no processo de optimização.

De um modo geral, verificou-se que os teores de sódio e de potássio nas amostras analisadas se encontram na gama de valores determinada por outros autores em estudos realizados com méis monoflorais produzidos noutros países. Os resultados permitiram estabelecer comparações entre diferentes tipos de mel monofloral produzido em Portugal.

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AVALIAÇÃO DA VITAMINA C NO SUMO DE MAÇÃ: ESTUDO COMPARATIVO DA APLICAÇÃO DE DIFERENTES MÉTODOS ANALÍTICOS

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A vitamina C, ácido ascórbico, é um micronutriente essencial à saúde que desempenha um papel fundamental no crescimento e desenvolvimento do ser humano. São-lhe atribuídas funções importantes em diversos processos biológicos, entre as quais se destaca a sua acção como antioxidante, que possibilita a eliminação de radicais livres resultantes do metabolismo celular e permite retardar os efeitos degenerativos do envelhecimento.

Em virtude de não poder sintetizar ácido ascórbico, o homem necessita de o ingerir com frequência, normalmente, através dos alimentos. No entanto, como não é aconselhável um consumo excessivo de vitamina C (a dose recomendada é de 60 mg/dia) torna-se imprescindível avaliar e controlar o teor deste composto em produtos alimentares e farmacêuticos. Existem actualmente vários métodos de análise, a maior parte dos quais se fundamenta nas características antioxidantes do ácido ascórbico. Contudo, continua a sentir-se necessidade de desenvolver um método simples, sensível e de baixo custo para aplicação em análises de rotina na indústria alimentar e farmacêutica.

Neste contexto, o presente trabalho tem como principal objectivo, o estudo comparativo da aplicação de três métodos analíticos, titrimetria, espectrofotometria no visível e voltametria de varrimento linear, na quantificação do ácido ascórbico num sumo de maçã comercial. Os ensaios realizados em titrimetria envolveram titulações iodométricas, com o amido como indicador e também titulações redox do ácido ascórbico com o 2,6-diclorofenolindofenol (DCIP). O método utilizado em espectrofotometria fundamentou-se na redução do complexo Cu(II)-NH_3 a Cu(I)-NH_3 a qual é acompanhada de uma diminuição de absorvência que pode ser seguida a 600nm. Finalmente, na técnica voltamétrica foi utilizada uma célula com um sistema de três eléctrodos, um eléctrodo de trabalho de platina, um eléctrodo de referência de Ag/AgCl e um eléctrodo auxiliar também de platina. Nesta técnica electroquímica é estabelecida uma corrente eléctrica entre os eléctrodos de trabalho e auxiliar, sendo medida a diferença de potencial

entre os eléctrodos de referência e de trabalho.

De um modo geral, os resultados obtidos através dos três métodos de análise apresentaram uma boa concordância com o teor em vitamina C referido pelo fabricante. O estudo efectuado mostrou a possibilidade de aplicação do método espectrofotométrico, desenvolvido para a análise de medicamentos, a amostras de sumo de maçã e permitiu comparar os três métodos em termos de simplicidade e rapidez de análise bem como em relação à sensibilidade, repetibilidade e ao rigor que permitem.

APLICAÇÃO DE TÉCNICAS VOLTAMÉTRICAS NA QUANTIFICAÇÃO DO ÁCIDO ASCÓRBICO EM SUMO DE MAÇÃ

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As vitaminas são compostas orgânicas que desempenham funções essenciais no metabolismo celular. O ácido ascórbico, vulgarmente conhecido como vitamina C, faz parte desse conjunto de compostos, ao qual é reconhecido um papel importante de protecção contra os efeitos nocivos de radicais livres.

Estas características antioxidantes permitiram o desenvolvimento de várias técnicas de análise para a determinação do teor em ácido ascórbico, nomeadamente, titulações de oxidação-redução, métodos espectrofotométricos e electroquímicos .

O objectivo deste trabalho foi o estudo comparativo da aplicação de duas técnicas electroquímicas, voltametria de varrimento linear e polarografia diferencial de impulsos na quantificação do ácido ascórbico em sumo de maçã de uma marca comercializada em Portugal. O método de análise tem como fundamento a reacção de oxidação do ácido ascórbico a ácido dihidroascórbico, a qual é realizada numa célula electroquímica com um sistema de três eléctrodos. Na voltametria foi usado como eléctrodo de trabalho um eléctrodo de platina, enquanto que na polarografia se utilizou um eléctrodo gotejante de mercúrio. Em ambas as técnicas, o eléctrodo de referência foi o de Ag/AgCl ($\text{KCl } 3 \text{ molL}^{-1}$), sendo o contra-eléctrodo de platina para a voltametria, e de carbono vítrio na polarografia.

As Figuras 1 e 2 exemplificam os resultados obtidos na análise do sumo de maçã através do método da adição de padrão.

O conjunto de voltamogramas (Figura 1) foi traçado aplicando um varrimento de potencial entre $-0,2$ e $+1,4$ V, com uma velocidade de 25 mVs^{-1} e apresentaram, em média, um potencial de pico, E_p , de aproximadamente $0,48$ V.

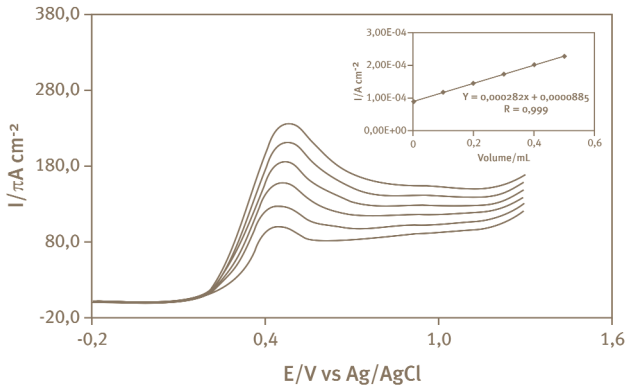


Figura 1 –Voltamogramas e respectiva curva de calibração.

Os polarogramas apresentados na Figura 2, foram obtidos em meio tamponizado, acetato de sódio/ácido acético, a pH 4,64 e traçados entre -0,025 e +0,16 V com uma velocidade de varrimento de 10 mVs⁻¹. O potencial de meia onda, $E_{1/2}$, foi encontrado para um valor de aproximadamente 0,088 V.

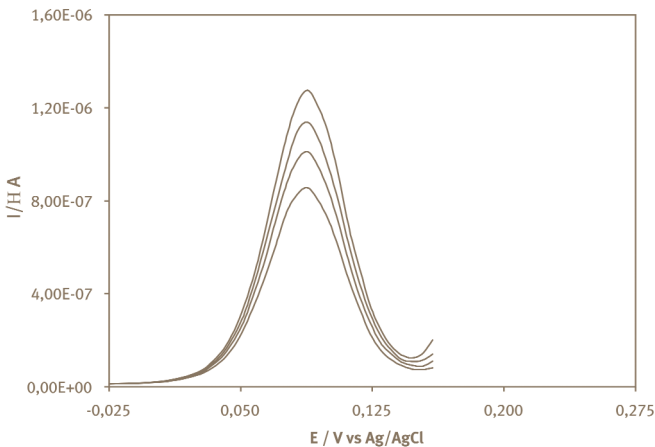


Figura 2 –Polarogramas e respectiva curva de calibração.

Os resultados obtidos apresentaram uma boa concordância com o teor em vitamina C referido pelo fabricante, e permitiram comparar as duas técnicas em termos de repetibilidade e exactidão.

DETERMINAÇÃO DO TEOR EM COMPOSTOS FENÓLICOS EM MEL NACIONAL

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O mel apresenta propriedades antioxidantes, as quais são resultantes da presença de compostos com essas características na sua composição. Os antioxidantes desempenham um importante papel na conservação dos alimentos, possibilitando a manutenção das suas propriedades durante mais tempo. São, também, essenciais à saúde uma vez que ao serem ingeridos com frequência, combatem as doenças degenerativas. Estudos recentes mostraram a existência de fenóis e flavonóides no mel os quais, juntamente com a prolina, contribuem para a actividade antioxidante deste produto.

Este trabalho surge no seguimento da caracterização físicoquímica de amostras de mel de origem nacional e tem como objectivo a quantificação dos compostos fenólicos através do método de Folin-Ciocalteu. Segundo este método, os grupos hidroxilo oxidáveis dos compostos fenólicos interactivam com o reagente de Folin-Ciocalteu, resultando uma coloração azul cuja intensidade foi medida a 760nm, num espectrofotómetro de UV-Vis ATI-UNICAM de duplo feixe. O doseamento foi efectuado através de rectas de calibração com ácido gálico.

Os resultados permitiram comparar a concentração em compostos fenólicos nas diversas amostras e avaliar a possível influência da origem botânica do mel nos teores observados.

SOLUBILITY OF ALKENES IN THE FERMENTATION MEDIUM OF XANTHOBACTER

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The solubility of gases in liquids is an important research area with a wide variety of applications, ranging from chemical process design to biotechnology and environmental sciences. On the other hand, the solubility studies on model systems, like simple hydrocarbons in water, are also important to test liquid theories and provide information on aqueous solutions structure and hydrophobic interactions.

Several authors reported the production of epoxides by several microorganisms, which are able to oxidize the gaseous alkenes like ethylene, propene and 1-butene. One of them is the *Xanthobacter* bacterial strain which is also able to resolve racemic mixtures of 2,3 epoxyalkanes to optically pure compounds. In this way, measurements of solubility of these alkenes in the aqueous growth medium of these bacteria will be important for the quantification of the fermentation processes. Furthermore, as the growth medium is an aqueous solution of different salts, a comparison with the alkenes solubility in water will provide information for the discussion of the salting-out effect.

The aim of this work was to carry out solubility measurements of ethylene, propene and 1-butene in the fermentation medium of *Xanthobacter* Py2 in the temperature range of 298.15-308.15K, which includes the optimal growth temperature of this strain (303.15K), and at atmospheric pressure. These studies are a part of an experimental program developed in our laboratory.

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*Livro de Resumos de
8th International
Chemical Engineering
Conference, Chempor
05, Coimbra, Portugal,
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A OCUPAÇÃO CIENTÍFICA DE JOVENS NAS FÉRIAS NO CENTRO DE ESTUDOS DE ENGENHARIA QUÍMICA DO ISEL

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da Divisão de Ensino
e Divulgação da
Química, Lisboa,
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2005.*

O Centro de Estudos de Engenharia Química (CEEQ) do Instituto Superior de Engenharia de Lisboa (ISEL) desenvolve, desde 1988, acções de colaboração entre a Escola e a comunidade, realizando actividades de I&D, formação e prestação de serviços. Actualmente o Centro é constituído por cinquenta e nove membros com qualificações em diversas áreas científicas. A partir de 2004, o CEEQ tem vindo a promover estágios de Ocupação Científica de Jovens nas Férias no âmbito de projectos de investigação nas áreas do Ambiente, Análise Química, Química Orgânica, Química Inorgânica e Tecnologia Química que se encontram em execução no Departamento de Engenharia Química do ISEL.

Na edição de 2004 realizaram-se sete estágios cujos temas foram:

- Análise de produtos do dia a dia;
- Análise de amostras ambientais;
- Em busca da vitamina C em sumos de fruta;
- Determinação dos teores de chumbo no solo da cidade de Lisboa;
- Acidez do iogurte. Como determiná-la?
- Preparação e caracterização de um polímero sintético;
- Reciclagem de plásticos por pirólise.

Nesta acção participaram onze investigadores e dezassete estudantes do 10.º e 11.º anos, os quais no final do estágio elaboraram um painel de divulgação do trabalho realizado. O modo com decorreu esta acção constituiu um forte incentivo para que, em 2005, fossem apresentadas onze propostas de estágios, segundo os temas:

- Na rota do sangue artificial: síntese de um modelo de hemoglobina;
- Os açúcares e os adoçantes nos alimentos;
- A qualidade da água que bebemos;
- A química que nos rodeia;
- Caracterização da poluição das águas residuais urbanas. O que remove uma ETAR?
- Estudo da reactividade de alguns metais;
- Determinação do teor alcoólico, em volume, de bebidas alcoólicas;
- O papel da refração da luz num processo de destilação;
- Medir a poluição pelo chumbo em Lisboa;

- Isolamento e caracterização dos pigmentos do espinafre;
- Preparação de um sabão a partir de gorduras animais e sua caracterização.

Na acção colaboraram dezoito investigadores e trinta alunos do 10^o, 11^o e 12^o anos de diversas escolas do país nomeadamente do Porto, Viseu, Santarém e Lisboa.

Os resultados da avaliação de ambas as edições dos estágios são motivadores para continuar a divulgar junto dos jovens a experimentação em Química.

O ELÉCTRODO DE FILME DE BISMUTO NA DETERMINAÇÃO DE METAIS TÓXICOS EM AMOSTRAS REAIS POR VOLTAMETRIA DE REDISSOLUÇÃO ANÓDICA DE ONDA QUADRADA

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Covilhã.*

O desenvolvimento de métodos e procedimentos para a detecção e determinação de metais tóxicos como o Cd(II) ou o Pb(II) em amostras ambientais reveste-se de particular importância face aos efeitos adversos que estes poderão exercer no meio ambiente e nos sistemas biológicos em geral.

A elevada sensibilidade e repetibilidade fazem da Voltametria de Redissolução Anódica de Onda Quadrada (SWASV) uma das técnicas mais populares neste tipo de análises. Os baixos limites de detecção que se conseguem alcançar com esta técnica são, em parte, determinados pelos parâmetros voltamétricos e demais condições experimentais utilizadas onde o tipo de eléctrodo de trabalho é, sem dúvida, um dos aspectos mais importantes.

Apesar do mercúrio ser um elemento extremamente atractivo como material de eléctrodo, devido a: elevada sobretensão de $H_2(g)$, superfície facilmente renovável e elevada repetibilidade (em função da amálgama reversível que forma com os metais presentes na amostra em estudo), algumas desvantagens devem ser tomadas em consideração. É o caso da sua elevada toxicidade e da sua bioacumulação em organismos vivos, solos ou sistemas aquáticos.

Seguindo uma tendência generalizada de eliminar o mercúrio dos ensaios analíticos, verifica-se um aumento na investigação de novos métodos e materiais de eléctrodo “mais amigos do ambiente”.

De entre vários materiais de eléctrodo alternativos, como ouro, carbono ou irídio, o bismuto parece ocupar um lugar de destaque por evidenciar uma performance favoravelmente comparável à do mercúrio no âmbito da SWAV, aliada à sua baixa toxicidade.

Neste trabalho testaram-se as potencialidades do bismuto como material de eléctrodo na análise de metais tóxicos em amostras ambientais por voltametria de redissolução anódica. Para tal foi efectuado um estudo de optimização dos parâmetros voltamétricos (potencial de deposição, tempo de deposição, frequência, impulso e amplitude de onda quadrada), bem como das demais condições experimentais (preparação das amostras para análise, espessura do filme de bismuto, electrólito suporte, etc.).

Uma vez otimizado o método voltamétrico procedeu-se à análise de amostras reais (solos e/ou folhas recolhidos na cidade de Lisboa), de modo a estudar a performance do eléctrodo de filme de bismuto em amostras de matriz complexa.

No final do estudo foi possível constatar-se que a utilização do bismuto como material de eléctrodo se apresenta como uma alternativa viável ao filme de mercúrio.

DETERMINATION OF PLATINUM GROUP ELEMENTS (PGE) IN LISBON SOILS

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The polluting metals of the environment represent a problem of public health. Until some years ago the lead and other heavy metals were the centre of the attention in terms of environmental analysis. With the abolition of the gasoline with lead, nowadays there are new concerns towards the metallic emissions originated by the catalyts in use in the automobile vehicles. Metals that were not considered dangerous as platinum, rhodium and palladium, are now preoccupying for the human health and for that is important to quantify its presence in the environment.

In this work is described the quantification of these metals in a urban environment, the soil of Lisbon city. Soils were collected in six places of the city of Lisbon, places subject to different intensities of automobile traffic. In each place 12 surface samples were collected (0-20 cm) distributed by three circumferences with rays of 1, 3 and 5 m, according to the direction of the 4 cardinal points. The soil was dry, drizzled and crushed in a mill of agate balls. Of each soil sample 2g are used for acid extraction of the metals (with *aqua regia*) microwave assisted. The rhodium determination was made by GFAAS and ICP-MS. In both determinations the respective analysis procedures were optimized. The determination of the rhodium is diffculted by the easiness that this metal forms oxides during the process of calcination of the solution. Also the matrix effects are omnipresent due to the complexity of the environmental samples.

It was verified that rhodium concentrations are directly proportional to the intensity of automobile traffic and, that in each place, the average concentration of the individual samples is identical to the concentration of a composed sample made from at least six individual random samples.

The determination of platinum and palladium is in development, foreseeing to present these results during the conference.

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III Congresso Ibero
Americano de
Contaminação e
Toxicologia Ambiental,
Setembro de 2005,
Cadiz, Espanha.*

GROWTH OF HIGH QUALITY (PER)₂M(MNT)₂ SINGLE CRYSTALS M=Au, Pt, Pd, Ni, Cu, Fe, Co

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The growth of high quality single crystals of the family (Per)₂M(mnt)₂ single crystals M=Au, Pt, Pd, Ni, Cu, Fe, Co has been a challenge for almost 30 years, limiting the study of this unique family of low dimensional conductors. In this paper we describe a systematic study of the crystal growth of these compounds by electrocrystallization under different conditions in order to optimise the results, with emphasis for the α phases of the Au and Pt compounds, where recently FICDW transitions were observed under high magnetic field.

The electrocrystallization process of synthetic metals is a complex process and its understanding is fundamental to the production of crystals of these compounds and also of a great variety of compounds and ordered molecular assemblies that are believed to be the future of nanoelectronics.

In electrocrystallization many factors interact and the most important are: solvent, electrodes, electroactive species, current or applied potential, support electrolyte and temperature.

Usually electrocrystallization of new materials is based in already known well succeed experiments that are improved. This was also the initial process we used to get to the optimal conditions for obtaining crystals: the use of a galvanostatic process with current density of 10 $\mu\text{A}\cdot\text{cm}^{-2}$, platinum electrodes, perylene and tetraalkylammonium salts of the metals as electroactive substances, dicloromethane as solvent and a temperature of 30°C. Even maintaining these conditions we obtained crystals of two different phases (α , β) identifiable by transport measurements.

The systematic study of the electrocrystallization conditions allowed to identify the determinant variables of the process and to minimize the obtention of several phases of the same compound.

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Crystalline Organic
Metals,
Superconductors, and
Ferromagnets,
National High
Magnetic Field
Laboratory, September
2005, Key West,
Florida, USA.*

COMPARAÇÃO DE MÉTODOS ICP – MS E GFAAS, NA DETERMINAÇÃO DE ELEMENTOS DO GRUPO DA PLATINA (PGE’S) NOS SOLOS DE LISBOA

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Os metais poluentes do ambiente já há muito tempo que representam um problema efectivo de saúde pública. Tradicionalmente a análise química a este nível verifica-se essencialmente ao nível de metais pesados como o chumbo, cádmio ou cobre. Actualmente, e depois da abolição da gasolina com chumbo, a atenção começa a centrar-se ao nível das emissões metálicas originadas pelo uso catalisadores nos veículos automóvel. Os metais constituintes dos catalisadores como platina, ródio e paládio (PGE’s), e emitidos por estes durante o seu funcionamento, são hoje em dia tidos como ameaças concretas e efectivas para a saúde humana. Na determinação destes metais deparamo-nos com principais dificuldades a baixa concentração destes metais e os complexos efeitos de matriz das amostras.

No presente trabalho estudou-se a amplitude da poluição causada pelos PGE’s nos solos da cidade de Lisboa. Foram recolhidas amostras de solos em seis pontos da cidade de Lisboa sujeitos a diferentes intensidades tráfego automóvel. Em cada local foram recolhidas doze amostras individuais. As amostras de solo foram sujeitas a um processo de digestão ácida com água régia, utilizando microondas com vista à extracção total dos metais.

A quantificação dos PGE’s foi efectuada por GFAAS e ICP-MS. A determinação do Ródio por GFAAS é dificultada pela facilidade que este metal tem em formar óxidos durante o passo da calcinação. A platina e o paládio, por se encontrarem em concentrações muito reduzidas, não puderam ser quantificados por GFAAS. Em ICP-MS, e após optimização exaustiva dos métodos de digestão e análise, foi possível a quantificação dos três metais.

Pode concluir-se que as concentrações do PGE’s nos solos são já mensuráveis e a sua concentração revela já alguma amplitude: Verifica-se também que são directamente proporcionais à intensidade de tráfego automóvel registado no local.

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É ainda de salientar que a optimização das condições operatórias e de análise para o método de GFAAS se revestiu de sucesso particular ao permitir a redução do tempo global de análise face a outros métodos descritos na bibliografia e para o mesmo tipo de aplicação

OPTIMIZAÇÃO DO PROCESSO DE EXTRACÇÃO SIMULTÂNEA DE METAIS DE SOLOS URBANOS

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O tráfego automóvel é responsável por um variado leque de emissões poluentes, nas quais se englobam metais como Cu, Pb, Pt, Pd e Rh. Nesta emissões o cobre provém da utilização do combustível, dos óleos lubrificantes e dos sistemas de travões; o chumbo, do sistema de travões e pelo desgaste da carroçaria, enquanto o desgaste dos catalisadores dos veículos automóveis é responsável pela libertação de Pt, Pd e Rh. Todos estes metais provocam danos na saúde dos habitantes, com particular ênfase nas grandes cidades onde a sua emissão é mais elevada.

Pretende-se, no âmbito do projecto em curso, quantificar o teor destes metais em solos recolhidos em zonas urbanas, nomeadamente em locais próximos de vias rodoviárias com elevado tráfego automóvel. Em Lisboa foram escolhidos os seguintes locais de amostragem: Marquês de Pombal, 2^a Circular e Calçada de Carriche. Para a garantia de uma correcta quantificação há que garantir que todos os metais presentes no solo sejam extraídos quantitativamente deste para sua posterior determinação.

A preparação das amostras consistiu em: secagem a 40 °C durante 24 h, limpeza de substâncias estranhas, peneiração a 2 mm, homogeneização e divisão das amostras, moagem em moinho de bolas de ágata, digestão ácida assistida por microondas e determinação dos teores em metais utilizando as técnicas de GFAAS e ICP-MS.

Com a realização deste trabalho pretendeu-se otimizar um processo de digestão que extraísse simultaneamente os vários metais em estudo, por não existir nenhum processo aceite por organizações internacionais, como a ISO ou a US-EPA, que concilie a extracção simultânea destes metais utilizando microondas de vaso aberto. Optou-se por tecnologia de vasos abertos porque neste processo, em oposição à extracção de vaso fechado, é possível a utilização de uma maior quantidade de amostra, necessária neste estudo em que também se pretende quantificar os PGE's (*platinum group elements* - platina, ródio e paládio) presentes em muito baixos teores (ver comunicação apresentada neste encontro por H. Silva). Os parâmetros otimizados foram: volume de reagente (água-régia), tempo de formação da água-

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régia, velocidade de aquecimento, temperatura de extracção e tempo de reacção.

A obtenção de uma combinação óptima destes parâmetros permitiu a determinação simultânea dos metais evitando assim a utilização de dois processos de extracção, um vocacionado para a extracção de Pt, Pd e Rh, e outro vocacionado para a extracção de Cu e Pb. Consegue-se assim a poupança de um precioso tempo de análise e a garantia do uso de um procedimento igual e independente na extracção dos solos do dois grupos de metais.

THE USE OF POLYOL-RESPONSIVE MONOCLONAL ANTIBODIES IN IMMUNOAFFINITY CHROMATOGRAPHY AND AS A PROBE FOR UNFOLDING OF WILD-TYPE AND ALTERED (T103I) AMIDASE FROM *Pseudomonas aeruginosa*

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Since immunoaffinity chromatography is a powerful protein purification technique of interest in proteomics, monoclonal antibodies (Mabs) against mutant (T103I) amidase from *P. aeruginosa* were raised by hybridoma technology. In order to identify Mabs that bind T103I amidase tightly but release under gentle conditions, hybridoma clones secreting polyol-responsive Mabs (PR-Mabs) were previously screened. Nearly 10% of ELISA assay-positive hybridoma produced clones secreting PR-Mabs with potential application as ligands for immunoaffinity chromatography. To select the optimal conditions for amidase elution, an ELISA-elution assay was carried out, with two of these clones (F6G7; E2A6). The dissociation of ag-ab complex required 10% of propylene glycol and either 0,25 M (NH₄)₂SO₄ or 0,25 M NaCl. The binding of purified Mab of IgM class (E2A6) to wild-type and mutant amidases was investigated by direct ELISA, which revealed that it recognised specifically a common epitope on both amidases. Conformational changes on antigen molecule were studied. Mab E2A6 showed a higher affinity for heat denatured forms than for native forms as revealed by affinity constants suggesting that the Mab recognizes a cryptic epitope. The effect of Mab E2A6 on amidase activity was also investigated. The binding of Mab to wild-type and mutant amidases exhibited an inhibition and activation of 60% as a function of time, respectively. This PR-Mab is useful as a probe to detect conformational changes in native and denatured amidases as well as a ligand in immunoaffinity chromatography, which is of great interest in protein purification and proteomics.

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SELECTIVE ADSORPTION OF MONOCLONAL ANTIBODIES AGAINST MUTANT AMIDASE FROM *Pseudomonas aeruginosa* ON TAILOR-MADE IMMOBILIZED METAL CHELATES

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Livro de Resumos da Conferência Internacional "Affinity 2005 – 16th Biannual Meeting of the International Society for Molecular Recognition (ISRM)", Resumo 825, pp 65, Uppsala, Suécia, 14-18 Agosto 2005.

The chromatographic behaviour of monoclonal antibodies (Mabs) of IgM class against mutant (T103I) amidase from *Pseudomonas aeruginosa* was investigated on immobilized metal chelates. The effect of ligand concentration, the length of spacer arm and the nature of metal ion were investigated on immobilized metal affinity chromatography (IMAC). Mabs against mutant amidase adsorbed to Cu (II), Ni (II), Zn (II), Co (II) and Ca (II)-IDA agarose columns. The adsorption of Mabs onto immobilized metal chelates was pH dependent because an increase in the binding of Mabs was observed as the pH was varied from 6,0 to 8,0. The adsorption of Mabs to metal chelates was due to coordination of histidine residues to metal chelates which are available in the 3rd constant domain of heavy chain (CH₃) of immunoglobulins since the presence of imidazole in the equilibration buffer abolished the adsorption of Mabs to the column packed with commercial IDA-Zn(II) agarose at pH 8,0. The combination of tailor-made stationary phases for IMAC and a correct design of the adsorption parameters permitted to devise a one-step purification procedure for Mabs of IgM class. Culture supernatants containing Mabs of IgM class against mutant amidase (T103I) were purified by IMAC Co (II) column at pH 8,0. The results presented in this work strongly suggest that one-step purification of Mabs of IgM class by IMAC is a cost-effective and process-compatible alternative to other purification schemes.

DIFFERENTIAL CHROMATOGRAPHIC BEHAVIOR OF SOME LIGNOLYTIC ENZYMES FROM WHITE-ROT BASIDIOMYCETES ON IMMOBILIZED METAL CHELATES

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The lignocellulosic materials are the most abundant on earth, which has attracted great attention for production of useful substrates from this waste (Volc and Kubatova, 1994; Takakura and Kuwata, 2003). The white-rot fungi (Basidiomycetes) have the ability to degrade lignocellulosic substrates by synthesizing several lignolytic enzymes of industrial and medical interest such as xylanases (EC 3.2.1.8), celulasas (EC 3.2.1.4), glucose 2-oxidase (EC 1.1.3.10), peroxidase (EC 1.11.1.7), pyra-nose 2-dehydrogenase, superoxide dismutase (EC 1.15.1.1), and laccase (EC 1.10.3.2). White rot fungi are believed to be the most effective lignin-degrading microorganisms in nature.

The overproduction of lignolytic enzymes (py-ranose 2-dehydroge-nase, glucose 2-oxidase, laccase, xylanases, and superoxide dismutase) from several fungal strains—(*Agaricus bisporus* (J.Lge) Imbach, *Trametes versicolor* (L.:Fr.)Pilat, *Ganoderma lucidum* (W.Curt.:Fr.) Lloyd, *Pleurotus ostreatus* (Jacq.:Fr.) P.Kumm., and *Fusarium* sp.)—was carried out by optimizing the composition of the culture media. As far as the composition of culture media is concerned, several agricultural wastes were used, such as rice husks, corn cobs, and rice bran. The effect of specific inducers for overproduction of enzymes was also investigated using these fungal strains.

In order to devise a simple and rapid one-step purification procedure for lignolytic enzymes, the chromatographic behavior of these enzymes (laccases, glucose 2-oxidase, and superoxide dismutase) on immobilized metal chelates was investigated as a function of pH, nature of metal ion, length of spacer arm, ligand concentration, and nature of matrix. The adsorption of enzymes was investigated by using Metal (II)_iminodiacetic acid metal chelates containing Cu (II), Ni (II), Zn (II), Co (II), and Ca (II) as a function of pH. The adsorption to immobilized metal chelates was pH dependent, as evidenced by the fact that high adsorption was observed at pH 8.0. The adsorption of enzymes on metal (II)_IDA chelates was due to the available histidine residues on enzyme molecules, shown by the fact that the addition of imidazole in the buffer system abolished the binding of enzymes to these columns.

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Once the experimental conditions of immobilized metal affinity chromatography (IMAC) for enzyme purification were optimized, they were purified in one step by IMAC on Cu(II)-IDA agarose column at pH 6.0 and 8.0 with a high recovery of enzyme activity as well as a high degree of purity. Purified preparations of enzymes were apparently homogeneous on native PAGE and SDS-PAGE. The differential chromatographic behavior of enzymes on metal(II)-IDA chelates is apparently due to the number and spatial distribution of available histidine residues on these enzyme molecules.

EXTRACTION OF SEVERAL INDUSTRIAL ENZYMES OF COMMERCIAL INTEREST FROM AN AGRICULTURAL WASTE

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The disposal of agricultural wastes is a major universal problem because it contributes substantially to environmental pollution. Some of these agricultural wastes are either fed to animals directly, discretely burnt or discarded. However, most agricultural wastes and by-products can be used to produce several components of commercial interest such as enzymes and secondary metabolites. Therefore, the present work was conducted in order to attempt to extract several enzymes from a well defined (but patent pending) agricultural waste by varying several parameters such as the nature of solvent for homogenization, pH, temperature and time of homogenization. The enzyme activities of the following enzymes were assayed in the supernatant: cellulase (EC 3.2.1.4), xylanase (EC 3.2.1.8), laccase (EC 1.10.3.2), beta-glucanase (EC 3.2.1.6) and an acidic protease. The results obtained revealed that all these enzymes were extracted from the agricultural waste by using ordinary tap water with agitation at room temperature. Furthermore, some of these enzymes were purified by immobilized metal affinity chromatography (IMAC) with high recovery of enzyme activity as well as a high degree of purity as judged by electrophoretic analysis. Present results strongly suggest that the extraction of these enzymes of commercial interest from this agricultural waste may constitute an economically viable process at industrial scale.

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A GESTÃO INTEGRADA DE RESÍDUOS SÓLIDOS URBANOS

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Tendo em conta a complexidade, diversidade e composição do lixo doméstico, bem como a sua gestão, tratamento e valorização, torna-se relevante a implementação de um Sistema Integrado de Resíduos Sólidos Urbanos (RSU) pelos sistemas públicos municipais ou multi-municipais de tratamento de RSU. Este sistema surge como o motor e peça principal que gere e faz funcionar todo um processo complexo mas eficaz, de gestão e tratamento das várias fileiras de RSU. Como exemplos pioneiros e inovadores em Portugal até agora, da implementação de um sistema integrado de RSU, podem-se tomar como referência o Sistema Integrado de RSU da Valorsul, o qual gere e trata os RSU de Lisboa, Loures, V. F. Xira, Amadora e Odivelas, com bastante sucesso desde 1994 e, o sistema integrado da Lipor II, que gere e trata os RSU da Área Metropolitana do Porto, nos concelhos de Espinho, Gondomar, Matosinhos, Maia, Porto, Póvoa de Varzim, Valongo e Vila do Conde.

O Sistema de Gestão Integrada de RSU actua, genericamente, em duas fases importantes:

Fig. 1: Etapas constituintes de um sistema integrado de RSU



Na fase de recolha, o sistema actua nas seguintes vertentes:

RECOLHA SELECTIVA DE MATERIAIS RECICLÁVEIS - Ecopontos + Ecocentro

RECOLHA SELECTIVA DE MATÉRIA ORGÂNICA - Recolha especializada

RECOLHA INDIFERENCIADA - Contentores tradicionais

Na fase de tratamento e deposição final de RSU, o sistema pressupõe a existência de unidades de valorização, tratamento (com recuperação de matéria e/ou de energia) e deposição controlada. Este conjunto de unidades pressupõe a hierarquia definida na lei no que concerne à gestão de quaisquer resíduos sólidos:



Fig. 2: Etapas hierárquicas da gestão de RSU

IMPACTES AMBIENTAIS ASSOCIADOS:

Em cada etapa deste sistema integrado, existem impactes ambientais associados, os quais devem ser contabilizados e analisados por forma a se ter, por um lado, conhecimento das melhores condições operatórias das várias unidades, por outro lado, estar de acordo com a legislação vigente em matéria de tratamento de RSU e de análise de impacte ambiental e, finalmente, mas não menos importante, assegurar um ambiente sustentável para toda a comunidade envolvente, nomeadamente as populações e o meio ambiente, que são os grandes beneficiados com a implementação deste sistema.

Como exemplo pioneiro e inovador da implementação de um sistema integrado de RSU, há mais de 10 anos em Portugal, tem-se o sistema integrado da Valorsul, esquematizado na figura seguinte:

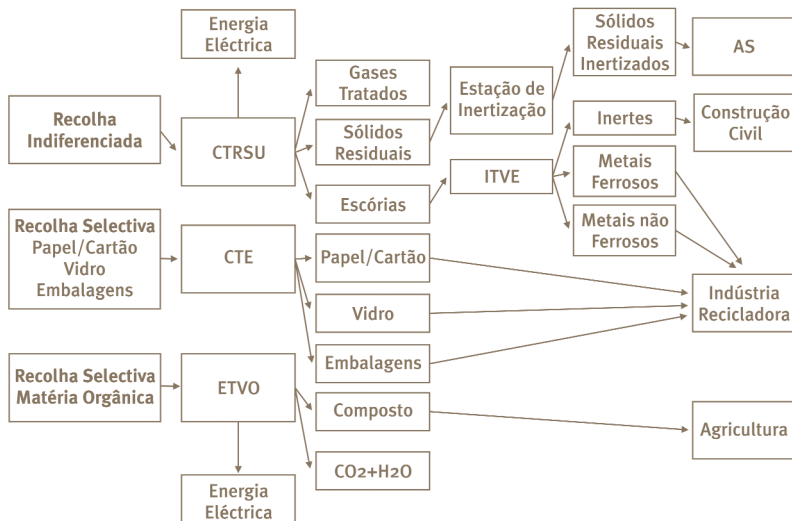


Fig. 3: Sistema Integrado de gestão e tratamento de RSU da Valorsul

VISCOSIDADE DE MISTURAS DE POLI(ETILINOGLICOL) 200 com CO₂ SUPERCRITICO NA GAMA DE 313-348 K e 0.1-25 MPa.

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A adição de um fluido supercrítico a um polímero altera as suas características, permitindo melhorar o processamento de materiais poliméricos, nomeadamente em operações de modificação, impregnação e extracção (Kazarian, 2000). A utilização de dióxido de carbono supercrítico como auxiliar de processamento de polímeros, devido à redução acentuada da viscosidade por efeito da sua adição, foi proposta por Gerhardt *et al.* (1994). Subsequentemente diversos autores empreenderam estudos de sistemas de poli(etilenoglicol) saturado com CO₂ supercrítico, sendo, contudo, escassos os trabalhos envolvendo directamente a relação entre a solubilidade do fluido supercrítico e a correspondente redução da viscosidade (Gourguillon e Nunes da Ponte, 1999).

No presente trabalho apresentam-se medidas de viscosidade de misturas de poli(etilenoglicol) 200 (PEG200) saturado com CO₂ supercrítico, na gama $313 \leq T \leq 348\text{K}$ e $0.1 \leq p \leq 25 \text{ MPa}$. As medidas de viscosidade foram efectuadas com um aparelho de fio vibrante, cujo equipamento e procedimento se encontram descritos por Gourguillon *et al.* (1998). Estes resultados são correlacionados com os dados experimentais de solubilidade obtidos para este sistema por Gourguillon e Nunes da Ponte (1999). Para este efeito, utilizou-se um modelo de volume livre (Kelly e Bueche, 1961) modificado (Bae, 1996, e Bae e Gulari, 1997), em conjunto com a equação de estado de Sanchez-Lacombe modificada (Sanchez e Lacombe, 1978 e Panayiotou, 1987). Para teste do modelo, este tratamento foi também aplicado ao sistema PEG400/CO₂, cujos dados foram anteriormente publicados (Gourguillon *et al.*, 1998).

A equação de Kelly-Bueche tem sido modificada por alguns autores, nomeadamente, Bae (1996) e Bae e Gulari (1997), para aplicação a misturas de polímeros com fluidos supercríticos, corrigindo o efeito da pressão no cálculo da fracção do volume livre. No presente trabalho, estudou-se a influência do método de cálculo do volume livre, na qualidade da correlação dos dados.

A equação de estado de Sanchez e Lacombe (EOS-SL) tem sido aplicada a misturas de polímeros com CO₂ supercrítico (Gerhardt *et*

al,1994, Garg *et al.*, 1994, e Gourgouillon e Nunes da Ponte, 1999). Em geral, esta equação tem sido aplicada a fluidos supercríticos utilizando apenas um parâmetro de interacção binária de correcção da regra de mistura da pressão característica. Neste trabalho optou-se pela utilização de dois parâmetros de interacção binária, corrigindo não só essa regra de mistura, mas também a do volume característico, conforme sugerido por Sanchez e Lacombe (1978) e Panayiotou (1987). Ambos os parâmetros de interacção binária foram obtidos a partir de dados experimentais da solubilidade publicados por Gourgouillon e Nunes da Ponte (1999). A aplicação da EOS-SL modificada foi, então, utilizada para determinar a densidade das misturas, e para calcular as composições de equilíbrio das fases, ou seja, para interpolar ou extrapolar os dados experimentais de solubilidade.

O PLANEAMENTO FACTORIAL EM UNIDADES PROCESSUAIS. CASO PRÁTICO

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Este trabalho tem por objectivo ilustrar a aplicação do planeamento factorial de experiências como ferramenta para a optimização de processos. O caso prático refere-se ao estudo de uma operação de extracção líquido-líquido, a operar em modo contínuo, em que se pretende remover o ácido benzóico presente numa mistura de isómeros de heptano (alimentação) para uma corrente aquosa (solvente).

A unidade de extracção líquido-líquido (GUNT CE620) é constituída por uma coluna de enchimento (anéis de Raschig de 10 mm) com 50 mm de diâmetro e uma altura de 1,5 m. Os factores , utilizados no estudo são o caudal de alimentação (mL/min) (A), o caudal de solvente (mL/min) (B) e a concentração de ácido benzóico na alimentação (g/L) (C). A variável de resposta é a concentração de ácido benzóico no extracto (g/L). Utilizou-se um planeamento factorial 2^3 com replicação. O modelo factorial completo pode ser escrito de forma simbólica como:

$$Y = \beta_0 + \beta_1 X_A + \beta_2 X_B + \beta_3 X_C + \beta_4 X_A X_B + \beta_5 X_A X_C + \beta_6 X_B X_C + \beta_7 X_A X_B X_C$$

Neste desenho trabalhou-se com um conjunto de três observações para cada combinação de níveis, apresentando-se os resultados obtidos no quadro 1.

Caudal de Solvente (B) (mL/min)	Caudal de Alimentação (A) (mL/min)			
	143		429	
	[ácido benzóico] alim (C) (g/L)			
	0,08	0,15	0,08	0,15
100	0,127	0,192	0,227	0,289
	0,117	0,177	0,216	0,315
	0,117	0,189	0,220	0,317
200	0,066	0,123	0,139	0,217
	0,062	0,099	0,156	0,239
	0,060	0,112	0,137	0,234

Quadro 1. Concentração de ácido benzóico no extracto

Para testar se os factores e interacções são significativos aplicou-se a técnica de análise de variância. Pode-se concluir que para $\alpha=5\%$, são significativos os factores A, B e C bem como a interacção AC. O modelo de regressão que permite estimar o valor de concentração de ácido benzóico no extracto em qualquer zona da região de experimentação é:

$$\hat{Y} = 0,1728 + \frac{0,1054}{2} X_A - \frac{0,0716}{2} X_B + \frac{0,0716}{2} X_C + \frac{0,0144}{2} X_A X_C$$

Para validar o modelo efectuaram-se três experiências confirmatórias. O modelo de regressão obtido pode ser usado para prever os valores de concentração de ácido benzóico no extracto (g/L), na região de experimentação.

IMPROVEMENT OF TOLUENE CATALYTIC COMBUSTION BY ADDITION OF CAESIUM ON COPPER EXCHANGED ZEOLITES

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Catalytic oxidation has been identified as one of the most important and promising processes to destroy VOCs at low concentration. Catalysts based on supported noble metals are very efficient for VOCs combustion, but they are relatively expensive. From the activity point of view, copper supported on different materials, namely on zeolites, have been suggested as potential catalysts and alternative to noble metals. In this work, HY and HMFI zeolites exchanged with copper (1-2 wt. %) and caesium (5-10 wt.%) have been studied in catalytic combustion of toluene (800 ppm) with air using WHSV of 24000 h⁻¹. The catalysts activity has been analyzed by comparison of light-off curves. The characteristics of catalysts and the state of copper ions in Cu-Y and CuMFI containing additions of Cs, were evaluated by XRD, adsorption/desorption of toluene followed by TG/DSC, H₂-TPR, and in-situ FTIR of NO adsorbed on copper ions. CuMFI based catalyst are more active for complete oxidation of toluene than CuY with similar copper contents. The light-off temperature (temperature at 50% toluene conversion into CO₂) determined for CuMFI is about 310^o C, while for CuY the temperature is 420^oC. In both Cu zeolites, the addition of Cs leads to a decrease of 50^oC in light-off temperatures. The addition of Cs provokes a decrease of capacity of adsorption of toluene, but it makes the desorption difficult, which is evidenced by an increase of desorption heat. The presence of Cs also affects the position of Cu²⁺ ions in zeolite matrix and its coordination geometry. Furthermore, an increase of reducibility of Cu²⁺ to Cu⁺ and Cu⁺ to Cu^o, occurred in CsCu zeolites. These results indicate that oxidation activity of copper ions supported on zeolites can be improved changing its coordination and location by the presence of bulky cations such as Cs.

DETERMINAÇÃO DO TEOR EM SÓDIO E POTÁSSIO EM MEL MONOFLORAL

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Amostras de mel de produção nacional e com diferente origem floral (trevo, incenso, rosmaninho e urze) foram caracterizadas em termos de teor em cinzas, pH e acidez total, índice de refração e teor em água, condutividade eléctrica e rotação específica. Os resultados da caracterização permitiram estabelecer comparações em relação às propriedades fisicoquímicas dos diversos tipos de mel e avaliar se esses parâmetros se encontram dentro dos limites recomendados. Em seguida e com vista ao doseamento dos elementos metálicos, as amostras de mel foram reduzidas a cinzas e efectuou-se a determinação do teor em sódio e em potássio por espectrometria de absorção atómica com uma chama de ar-acetileno. De um modo geral, todos os méis analisados apresentaram teores de potássio superiores aos de sódio, evidenciando o mel de urze o maior teor em potássio e o de rosmaninho o menor teor em sódio.

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2005.*

AVALIAÇÃO DA VITAMINA C NO SUMO DE MAÇÃ: ESTUDO COMPARATIVO DA APLICAÇÃO DE DIFERENTES MÉTODOS ANALÍTICOS

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Foram analisadas várias amostras de diferentes lotes de uma marca de sumo de maçã, comercializado em Portugal, com a finalidade de comparar a aplicação de três métodos analíticos, titrimetria, espectrofotometria no visível e voltametria de varrimento linear, na quantificação da vitamina C. Estes métodos foram inicialmente aplicados na determinação da concentração em ácido ascórbico numa solução padrão, sendo o método voltamétrico o que conduziu a uma maior exatidão, com um erro associado de apenas 0,6%. Na análise do sumo de maçã, os três métodos apresentaram uma boa repetibilidade, uma vez que os valores do desvio padrão dos resultados foram inferiores a 8 mg/L. No entanto e como seria de esperar, ao serem aplicados na análise de amostras provenientes de diferentes lotes foram encontrados maiores desvios, nomeadamente em relação ao método espectrofotométrico, sendo o método voltamétrico o que conduziu a um conjunto de resultados com uma menor incerteza associada.

SOLUBILITY OF ALKENES IN THE FERMENTATION MEDIUM OF XANTHOBACTER

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Solubility measurements of ethylene, propene and 1-butene in the aqueous growth medium of a *Xanthobacter* strain were carried out in a Ben-Naim type apparatus at the atmospheric pressure and in the temperature range of 298.15-308.15K. From the experimental quantities, the Ostwald coefficients, the mole fractions of the dissolved gases and the Henry coefficients were calculated using an iterative procedure and applying the non-ideality corrections for the vapour and liquid phases. The temperature effect on the gases solubility was discussed using the Clarke-Glew-Weiss equation and calculations of the standard molar Gibbs energy, enthalpy and entropy changes for the process of transferring the solute molecules from the gaseous phase to the cultivation medium were also performed. Comparisons were made with the alkenes solubility in water, showing that all these gases are about 2.5% less soluble in the bacteria growth medium.

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THE INFLUENCE OF VOLUMETRIC EQUIPMENT IN THE CHARACTERIZATION OF SOILS SAMPLES

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The quality and reliability of analytical results are depending on the experimental method, the operator, the reagents and also the measurement instruments in which the volumetric equipment are always included.

Volumetric measurement is critical in any analytic laboratory especially in situations were a small mistake in the volume measurement can cause a large error in the final results and in the yield of a reaction. In order to identify and reduce possible errors in intensive liquid handling process analysis it's necessary to calibrate the volumetric equipment used in the laboratory.

In the determination of the volume in the calibration of volumetric equipment the gravimetric method is used. The calibration results are determined at the temperature of 20 °C and expressed in millilitres contained in a flask, a pycnometer or a cylinder or flowed in case of burettes and pipettes.

The use of glassware recently calibrated is no doubt the ideal situation. However time (synonym of money) spent in the calibration procedures is considerable.

In our laboratory are made measures of heavy metals in soils of the city of Lisbon. To determine heavy metals in soils we use an acid digestion microwave assisted followed by an analysis of the metals through atomic absorption with graphite furnace. During the analysis process several glassware is used. We can use recently calibrated glassware (ideal situation) or, as an alternative, common class A glassware.

To compare the importance of using calibrated, with that of using non calibrated class A glassware, several tests were made in which these kinds of glassware were used in parallel. A series of condition tests were preformed in glassware to evaluate the influence of temperature and operator in the volume measurements.

The uncertainties of the results of the analysis using both kinds of glassware (calibrated and class A) were calculated. To calculate the uncertainties the methodology suggested by ISO was used. Because of the complexity of this task, and considering the high number of

uncertainty sources present in a real chemical analysis as that of a soil analysis, was used a Visual Basic application developed by us, already tested and validated.

MODULATED STRUCTURE OF [FeCl(DMPE)₂(NCC₆H₄NO₂)] [PF₆] A MATERIAL FOR USE IN NLO

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It is well known the recent interest in the nonlinear optical (NLO) properties of organometallic complexes. Most efficient NLO active complexes have a dipolar composition, with an electron-donating group linked by a π -conjugated bridge to an electron-accepting group. Our studies on complexes with this composition have been focused on metal *s*-nitriles, for which the second-order NLO responses have been determined. Since, it is also of interest to assess the importance of co-ligands in the donor metalcoordination sphere, our attention has turned to an alternative coordinated Fe(II) system, namely trans-chloro(diphosphine)iron nitriles. In the solid state our main interest is to align the molecules and avoid centrosymmetric space groups. When trying to solve the structure of the title complex we had several difficulties and the structure proved to be modulated. Refinements are being done using JANA and final results will be presented in this work.

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2005, A61, C476.

FROM CARBOXYLIC PRECURSORS TO THIOXANTHENES: INTERPLAY OF HYDROGEN BONDS, Br...Nitro, S...Carbonyl AND π ... π STACKING INTERACTIONS

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Recently large effort has been set into the synthesis of helical molecular systems, such as sterically overcrowded alkenes. These can be used as photorefractive materials as they allow the presence of measurable dipolar and magnetic contributions to NLO effects. The helical environment is due to the presence of bulky substituents causing sufficient hindrance between the upper and lower half of the alkene to enforce a helical distortion. We present here the results obtained in the precursors and thioxanthene used as basic templates. A systematic study of the intra and inter hydrogen bonds and intermolecular interactions is presented, due to its relevance in the folding and packing of the molecules.

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MICROWAVE-ASSISTED SYNTHESIS OF TRIS(PYRAZOLYL)METHANES, AN IMPROVED PREPARATIVE METHOD

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Herein we report a convenient microwave-assisted synthesis of hydrotris (1-pyrazolyl)methane which, by taking advantage of this alternative and efficient source of energy, greatly shortens the reaction times (from three days to one hour) and leads to an improved product yield.

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2005.*

AVALIAÇÃO DO POTENCIAL METANÓGENICO DE RESÍDUOS ORGÂNICOS

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Determinou-se o potencial metanogénico de resíduos sólidos biodegradáveis, nomeadamente frutas, vegetais e relva, utilizando cinco misturas pré-seleccionadas. Os diferentes tipos de resíduos apresentaram teores de sólidos totais de ca. 10-30% e cerca de 84-88% de sólidos voláteis. Da análise do volume de biogás produzido constatou-se que as misturas constituídas por 50, 75 e 100% de relva conduziram às produções mais elevadas de metano (257, 216 e 128 mL de CH₄/g de SV adicionado). Estas misturas produziram um biogás com 55-75% de metano. A taxa de produção de metano é discutida tendo por base diversos parâmetros de controlo do processo.

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Proceedings of the 9th International Chemical Engineering Conference (ISBN 972-8055-13-7), Coimbra, Portugal, 2005.

COPOLYMERISATION KINETICS OF A DIVINYLBENZYL *p*-TERT-BUTYLCALIX[4]ARENE DERIVATIVE AND STYRENE DETERMINED BY FT-IR SPECTROSCOPY

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Publicado em:
Proceedings of the 9th International Chemical Engineering Conference (ISBN 972-8055-13-7), Coimbra, Portugal, 2005.

In recent years, a growing interest as emerged in the field of polymeric materials containing calixarenes, regarding their potential usefulness as sensors, non-linear optic materials and devices for selective sorption of ions and neutral molecules. Calixarenes are a well-known class of synthetic receptor macrocyclic molecules, and its synthesis and applications have been comprehensively reviewed.

Our previous work in this area showed the ability of a monovinylcalixarene derivative, 25,26,27-tripropoxy-28-(4-vinyl-benzyloxy)-*p*-tert-butylcalix[4]arene (**1**), to be copolymerised with styrene (**St**), using the suspension polymerisation technique, with conversions up to 60% after 24h of reaction. It was found, from the ¹H NMR integrals corresponding to the former monomers, that the composition of the copolymers thus prepared showed a good correlation with the feeding ratios, which was interpreted as a result of the similar reactivity of the monomers involved. The tethering of two benzyl-vinyl units to the calix[4]arene core was then envisioned with the aim of render the monomer the ability to function as a brancher, a crosslinker agent, or even linearly cyclocopolymerise. Thus, when the radical polymerisation of styrene was carried out in the presence of the new bifunctional calix[4]arene monomer **2**, bearing two *syn*-distal vinyl polymerisable groups in the lower rim, new soluble and crosslinked polymeric materials were obtained. In particular, a soluble copolymer with a molar composition of *ca.* 1:13 (**2:St**; ¹H NMR analysis) was obtained under suspension polymerisation conditions at 82°C using toluene as porogen and acacia powder as stabiliser, when a molar feed ratio of calixarene **2** to **St** of 1:20 was used. This result clearly pointed to a fairly higher reactivity of the comonomer **2** as compared to styrene. A cyclopolymerisation route was postulated to account for the results, involving as propagating steps an intramolecular addition between the two-benzylvinyl pendant groups and an intermolecular step of the resulting radical with either a calixarene or a styrene monomer.

The present work was undertaken to further elucidate the reactivity of monomer **2** and its monoene counterpart **1** with styrene under conditions of solution polymerisation and thus shed same light to the aforementioned proposal.

ISOMERIZATION OF N-HEXANE OVER Pt-Ni/HBEA. THE INFLUENCE OF THE PREPARATION METHOD OF THE BI-METALLIC CATALYSTS

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The influence of the preparation method of bi-metallic catalysts Pt-Ni/HBEA has been studied in the reaction of n-hexane hydroisomerization and the results were compared to those obtained with the zeolites containing only Pt or Ni. The metal function was characterized by Temperature Programmed Reduction of H₂ and the catalytic reaction hydrogenation of toluene.

The results obtained in the hydroisomerization of n-hexane showed that the highest conversion and increased selectivity in di-branched products was obtained for the bi-metallic catalysts prepared by ion exchange with simultaneous addition of both Pt and Ni. The effect on the selectivity was particularly relevant when the ion exchange was performed at 80°C, which evidences that the interaction between the two metals was best achieved at higher temperature.

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2005*

THERMOCHEMISTRY OF 1-BROMOADAMANTANE IN BINARY MIXTURES OF WATER-APROTIC SOLVENT

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Solution enthalpies of 1-Bromoadamantane in the mixed solvents water-N,N-dimethylformamide, water-N,N-dimethylacetamide and water-acetone, were determined at 298.15 K, within the range of solubility of 1-Bromoadamantane in the mixed solvents.

The value for the solution enthalpy of 1-Bromoadamantane in water was determined based on extrapolation from the three mixtures. The solution enthalpies of transfer from the mixed solvents to cyclohexane were calculated. The effect of the composition of the mixtures on the thermochemical values obtained was also investigated.

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de 2005*

COMPARISON BETWEEN CORIANDER VOLATILE OILS OBTAINED BY SUPERCRITICAL CO₂ EXTRACTION AND HYDRODISTILLATION

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Supercritical fluid extraction (SFE) with CO₂ of volatile oil from coriander (*Coriandrum sativum* L.) seeds was carried out at the temperature of 40°C and pressures up to 150 bar with a flow apparatus using a two stage fractional separation technique.

Two ecotypes growing in different environmental conditions, one from Spain and the other from Italy, were studied. The best conditions of extraction (90 bar and temperature of 40°C), and separation (pressure of 70bar and temperature of -8°C, in the first separator, and a pressure of 20bar and a temperature of -5°C, in the second one), were used to assess the effect of different mean particle size.

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 seeds influence the yield and the composition of the oil in SFE. The coriander oil was analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The main compounds identified in the oils were a-pinene (2.5%), myrcene (1.7%), linalool (74%), camphor (3.3%), geraniol (3%) and geranylacetate (1.3%).

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SUPERCRITICAL CO₂ EXTRACTION OF SECONDARY METABOLITES FROM *Agaricus blazei*. EXPERIMENTS AND MODELLING.

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The mycelium and young fruiting bodies of *Agaricus blazei* were submitted to supercritical CO₂ extraction, in a modified commercial flow apparatus, at temperatures from 40 to 80 °C, pressures up to 600 bar and flow-rates from 2.0 to 9.0 g CO₂.min⁻¹.

The best extraction conditions of secondary metabolites, whereby the degree of solubilization (g extract/100 g of fungi) is the highest, was obtained with pure CO₂ at 400 bar, 70 °C and a flow rate of 5.7g CO₂.min⁻¹.

In order to increase the extraction yield of secondary metabolites, which are mostly present in glycolipid fractions, a polar compound (ethanol) was used as co-solvent in the proportions of 5 and 10 % (mol/mol). The presence of ethanol increased the yield when compared with the extraction with pure CO₂. Moreover, a simple model was applied to the supercritical CO₂ extraction of secondary metabolites from *Agaricus blazei*.

BIOCATALYSIS OF GLUCOSE 2-OXIDASE FROM *coriolus* *versicolor* AT HIGH PRESSURES

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Glucose 2-oxidase (pyranose oxidase, pyranose:oxygen-2-oxidoreduc-tase, EC 1.1.3.10) from *Coriolus versicolor* catalyses the oxidation of D-glucose at carbon 2 in the presence of molecular oxygen producing D-glucosone (2-keto-glucose and D-arabino-2-hexosulose) and hydrogen peroxide. This enzyme was used to convert D- glucose into D-glu-cosone at high pressures with compressed air in a modified commercial batch reactor. Several parameters affecting biocatalysis at high pres-sures were investigated as follows: pressure, enzyme concentration, glucose concentration, supercritical fluid and the presence of catalase. Glucose 2-oxidase was purified by immobilized metal affinity chro-matography on epoxy-activated Sepharose 6B-IDA-Cu(II) column at pH 6.0. The conversion of D-glucose into D-glucosone was dependent on the pressure since an increase in the pressure with compressed air resulted in higher rates of conversion. On the other hand, the presence of catalase increased the rate of reaction which strongly suggests that hydrogen peroxide inhibited the rate of reaction. The rate of conver-sion of D-glucose into D- glucosone by glucose 2-oxidase in the presence of either nitrogen or supercritical CO₂ at 110 bar was very low compared with the use of compressed air at the same pressure.

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2005.*

CORROSION BEHAVIOUR OF ALUMINIUM ALLOYS PRE-TREATED WITH BIS-[TRIETHOXYSILYLPROPYL] TETRASULPHIDE SOLUTIONS DOPED WITH $\text{Ce}(\text{NO}_3)_3$

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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 before painting increase their corrosion performance.

This work aims the evaluation of the corrosion resistance of a pre-treatment based on bis-[triethoxysilylpropyl] tetrasulfide (BTESPT) doped with cerium nitrate on aluminium alloy substrates. Electrochemical impedance spectroscopy (EIS) and Scanning Vibrating Electrode Technique (SVET) were used to evaluate corrosion resistance during immersion in NaCl solutions. Atomic Force Microscopy (AFM) was used to characterize the morphology evolution of dopped silane films. The results show that the pre-treatment provides excellent corrosion protection to the substrates and that the dopping with small amounts of cerium nitrate leads to a satisfactory “self healing” effect. Furthermore, the results evidence improved protection comparatively to the BTESPT only pre-treatment, both for Al 1050 and AA2024-T3.

INFLUENCE OF THE DEPOSITION PARAMETERS ON THE PROPERTIES OF BIS-[TRIETHOXYSILYLPROPYL] TETRASULPHIDE (BTESPT) LAYERS ON AA2024-T3 – AN ELLIPSOMETRIC STUDY.

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A bis-sulphur silane (BTESPT) was used to produce thin protective layers on AA2024-T3, a structural aluminium alloy widely used in the aeronautic industry, being the coatings analysed *ex-situ* by ellipsometry. Despite a slight degree of film anisotropy evidenced by measurements at different angles of incidence, an optical model of a single homogeneous phase could be employed to describe the silane based layer. The information obtained allowed to characterize the influence of the operational deposition parameters on the film thickness and structural organization of the silane phase (evaluated by its optical absorption). It is shown that the silane concentration of the solution and immersion time determine the final thickness of the formed layer while the curing time does not affect significantly this parameter. On the other hand, it was observed a marked decrease of the optical absorption of the coatings submitted to curing temperatures of at least 100°C, which should be ascribed to a structural reorganization phenomena induced by the removal of water molecules from the film. The data gathered by ellipsometry were successfully corroborated by independent surface profilometry analysis of the films.

Publicado em:

Materials Science Forum, 514-516 (2006) 682 (Proceedings of MATERIALS 2005, XII Portuguese Materials Society Meeting, III International Materials Symposium, 20-23 March 2005, Aveiro, Portugal).

AN ENERGY INTEGRATION TOOL FOR BATCH PROCESS

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Process integration is widely applied to continuous process. Among different methodologies, Pinch Analysis, with a thermodynamic basis is generally used due to it is easy implementation. The basic concepts of Pinch Analysis were therefore extended in this work to a batch process. The software developed, *BatchHeat*, highlights the energy inefficiencies in the process and thereby enables to set the scope for possible heat recovery, through direct heat exchange or storage. The *BatchHeat*, was applied to a case study as a first tool to get the targets for the heat exchanger network design. The results obtained show the enthalpy behaviour of the process and define an upper bound for direct heat transfer, thus suggesting different energy recovery projects. These alternatives were further compared and discussed.

UTILIZAÇÃO DO DESENHO DE EXPERIÊNCIAS NO ESTUDO DE OPERAÇÕES DE SEPARAÇÃO – APLICAÇÃO À EXTRACÇÃO LÍQUIDO-LÍQUIDO

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Melhorar a qualidade dos produtos e processos produtivos a um custo reduzido representa um desafio económico e tecnológico para os engenheiros. O desenho de experiências revela uma grande utilidade para alcançar esses objectivos. A sua aplicação a trabalhos laboratoriais facilita a aprendizagem deste tipo de ferramentas estatísticas potenciando a sua futura utilização pelos recém licenciados.

No caso particular da extracção do ácido benzóico de uma mistura de isómeros de heptano usando água como solvente num processo descontínuo, o desenho de experiências permitiu identificar as variáveis mais importantes e determinar um modelo de regressão para estimar o tempo necessário para extrair 50% do ácido benzóico presente na alimentação.

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CONTROLO GEOMÉTRICO DE SISTEMAS TUBULARES EM CONTRA-CORRENTE

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Portugal.*

Neste trabalho generalizam-se técnicas de controlo geométrico para sistemas tubulares de parâmetros distribuídos em contra corrente. A sua aplicação permite obter uma lei distribuída geral, de realimentação de estado, que garante uma dinâmica linear estável, em malha fechada, entre a entrada de referência e a saída a controlar. A lei é interpretada recorrendo a conceitos de geometria diferencial. É apresentada ainda uma aplicação a um reactor tubular com aquecimento em contra-corrente.

ADAPTIVE RECEDING HORIZON CONTROL OF TUBULAR BIOREACTORS

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This paper presents a case study of application of an adaptive non-linear predictive control algorithm to tubular bioreactors. According to the control strategy proposed, the system of PDEs describing the reactor is approximated by a lumped parameter model obtained using the Orthogonal Collocation Method. An adaptive receding horizon controller is then designed using Control Lyapunov Function methods. The design procedure and the resulting performance is illustrated by simulations in a two reactions model with Contois kinetics.

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IEEE Conference on
Decision and Control
and European Control
Conference ECC ,
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Xplore (Conference
Proceedings).*

ADAPTIVE RECEDING HORIZON CONTROL OF A DISTRIBUTED COLLECTOR SOLAR FIELD

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and European Control
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Xplore (Conference
Proceedings).*

This paper presents an adaptive receding horizon control algorithm for a distributed collector solar field which explicitly explores its distributed parameter character. The plant considered is a distributed collector solar field, being described by a nonlinear hyperbolic partial differential equation (PDE) which models the temperature dynamics. A lumped parameter model is obtained by applying Orthogonal Collocation. This model is then used as a basis for controller design. Stability is ensured for the lumped parameter model by resorting to Control Lyapunov function methods. Simulation results using a detailed physically based simulator of the solar field are provided.

CONTROLLING DISTRIBUTED HYPERBOLIC PLANTS WITH ADAPTIVE NONLINEAR MODEL PREDICTIVE CONTROL

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A number of plants of technological interest include transport phenomena in which mass, or energy, or both, flow along one space dimension, with or without reactions taking place, but with neglected dispersion. These types of processes are described by hyperbolic partial differential equations and are receiving an increasing attention in what concerns the application of Predictive Control. Two examples considered are distributed collector solar fields and tubular bioreactors. In both cases the manipulated variable is assumed to be the flow. For lack of space, only the first example is considered hereafter.

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Proceedings of "International Workshop on Assessment and Future Directions of Nonlinear Model Predictive Control", NMPC05, August 26-30, 2005, Germany.

ANALYSIS OF PROCESSING SYSTEMS INVOLVING REACTION AND DISTILLATION: THE SYNTHESIS OF ETHYL ACETATE

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CHEMICAL ENGINEER-
ING CONFERENCE,
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The integration of reaction and separation into a single process unit, i.e., reactive distillation, may offer several advantages over conventional systems that use a reactor followed by a distillation column. In this paper we explore the operational characteristics of reactive distillation and highlight some of its potential benefits, using the production of ethyl acetate as an illustrative example. With this aim, the two types of systems are compared employing different reactor types and a number of performance indicators, such as yield, conversion, purity, specific energy consumption and residence time. A sensitivity analysis is carried out on some variables and parameters, in order to explore and define the distillation columns operating conditions. As expected, results point to a clear advantage of reactive distillation, allowing for the azeotrope to be surpassed and for the overcoming of chemical equilibrium, favouring an increase in conversion and product purity, along with reduced operating costs.

SIMULAÇÃO DO COMPORTAMENTO DINÂMICO DE REACTORES TUBULARES

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A tubular reactor, with axial diffusion and Aris boundary conditions, employed to perform a first-order chemical reaction, is dynamically modelled by a series of continuous stirred tank reactors, the number of which depends on the operating conditions at steady state. The corresponding system of ordinary differential equations can be formally integrated in time, for an admission concentration represented by a staircase-like function. The resulting formulae are presented, as well as plots of data generated by a MATLAB function that uses them to perform the necessary calculations.

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ChemPor2005,
Setembro de 2005,
Coimbra, Portugal.*

SÍNTESE DE COMPOSTOS DERIVADOS DE FERRO(II) COM POTENCIAIS PROPRIEDADES EM ÓPTICA NÃO LINEAR

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Doutoramento em: Química

Grau Concedido por: Universidade de Évora

Orientadores: Maria Paula Alves Robalo

Provas Concluídas em: 26 de Janeiro de 2005

A Óptica Não Linear (NLO) é uma área da óptica que estuda as interações de campos magnéticos intensos da luz com a matéria para obter uma radiação emitida com novas características. A sua importância tecnológica tem impulsionado a investigação nesta área conduzindo ao design e síntese de novos materiais.

Nesta tese apresenta-se a síntese e caracterização de compostos organometálicos derivados de ferro(II), coordenados h_5 a um anel de ciclopentadienilo ou de indenilo; a síntese e caracterização, bem como a determinação das propriedades de óptica não linear, de compostos octaédricos de ferro(II), e também a síntese e caracterização de novos ligandos orgânicos utilizados para coordenar ao átomo de ferro(II).

RECOMBINANT WILD-TYPE AMIDASE FROM *Pseudomonas aeruginosa* PURIFICATION FOR SYNTHESIS IN DIFFERENT MEDIA. STRUCTURE-FUNCTION RELATIONS.

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Doutoramento em: Tecnologia Bioquímica

Grau Concedido por: Faculdade de Ciências da Universidade de Lisboa

Orientadores: Amin Karmali

Co-orientador: Maria Luísa M. Serralheiro

Provas Concluídas em: 28 de Outubro de 2005

A utilização de enzimas como catalisadores em reacções de síntese de compostos de interesse industrial tem recebido considerável atenção devido às amplamente conhecidas vantagens que os enzimas apresentam face a catalisadores químicos. Vantagens que vão desde a estereoespecificidade, a elevada especificidade para com o seu substrato, baixo consumo energético, a reutilização do biocatalisador e boa bioconversão. Deste modo, a biocatálise tem vindo a tornar-se uma alternativa aos métodos de síntese química de alguns produtos de importância.

Amidases (E.C. 3.5.1.4.) são enzimas que na natureza catalisam a hidrólise de ligações amida em amidas alifáticas primárias. Existindo em várias bactérias e fungos como *Pseudomonas* sp. e *Aspergillus* sp. onde estão envolvidos na redução dos compostos azotados orgânicos e na produção de amónia.

Amidases microbianas, que catalisam a hidrólise de amidas com formação do respectivo ácido e amónia, têm suscitado um interesse crescente em campos tão diversos como a neurobioquímica, a fisiologia das plantas e na microbiologia aplicada na produção à escala industrial de vários produtos de interesse no mercado. As vantagens da utilização deste enzima estão não só relacionadas com a possibilidade de catalisar inúmeras reacções, mas também com a ampla gama de substratos do enzima.

O objecto de estudo deste trabalho foi a amidase alifática (acilamida-amidohidrolase, EC 3.5.1.4) de *Pseudomonas aeruginosa* que catalisa a hidrólise de amidas primárias alifáticas, como a acetamida e propionamida. No entanto, este enzima catalisa também a hidrólise de pequenos ésteres alifáticos, apesar de a velocidade destas reacções ser bastante inferior à velocidade de hidrólise das amidas. Para além destas reacções de hidrólise, este enzima catalisa ainda reacções de transferase, transferindo o grupo acilo de amidas (transamidação), ácidos ou esters para a hidroxilamina. Os produtos finais desta reacção são os ácidos hidroxâmicos conhecidos pelas suas propriedades quelantes com vastas aplicações em medicina, agronomia, tratamento de efluentes, tecnologia nuclear e também na indústria

alimentar e de detergentes.

Apesar do enzima ter vindo a ser estudado e explorado há já vários anos, numerosas características estão ainda por investigar.

O conhecimento da natureza e do carácter do enzima torna-se inevitável ao ponderar a possível aplicação da amidase em algumas áreas de importância.

O objectivo deste trabalho revelou a necessidade do desenvolvimento de uma estratégia de purificação do enzima amidase que permitisse uma rápida purificação com elevado rendimento de modo a poder ser utilizado nos estudos a desenvolver.

A amidase nativa da *Pseudomonas aeruginosa* produzida numa estirpe recombinante JM 109 de *Escherichia coli* foi utilizada como a fonte da amidase nativa (wild-type). Esta estirpe tem clonado o gene da amidase nativa de *Pseudomonas aeruginosa* 8602.

No entanto, um elevado nível de expressão da amidase recombinante levou á agregação e acumulação do enzima na célula sob a forma de corpos de inclusão. Os efeitos das condições do crescimento na formação de corpos de inclusão pela estirpe de *Escherichia coli*, foram investigados combinando actividade enzimática com Espectroscopia de infravermelho por transformadas de Fourier (FTIR). O rendimento mais elevado na produção de enzima solúvel foi obtido seguindo condições subóptimas para induzir o crescimento. Observou-se ainda que o uso de etanol no meio de cultura levou a uma elevada produção do enzima, mas agregando quantitativamente sob uma forma que se revelou biologicamente activa. Os resultados demonstraram também que a agregação da amidase in vivo pode ocorrer na ausência de grandes alterações na estrutura secundária da proteína.

Um método simples baseado na espectroscopia de FTIR foi desenvolvido para o ensaio da actividade da amidase. Este ensaio contínuo envolve a detecção e quantificação dos substratos e produtos da reacção, em simultâneo.

O estudo cinético da reacção de hidrólise de vários substratos e também da sua reacção de síntese em meio aquoso foi realizado usando o método de quantificação de actividade desenvolvido utilizando espectroscopia de FTIR. Os resultados revelaram que a amidase demonstra maior actividade quando utiliza substratos de cadeia curta comparativamente a substratos ramificados ou aromáticos.

A interacção destes substratos com o enzima foi objecto de estudo usando a diferença entre os espectros de FTIR adquiridos durante o desenvolvimento da reacção com o enzima, de modo a monitorizar a reacção in situ. Esta metodologia evidenciou a presença de diferentes estruturas do substrato na mistura reaccional e o enfraquecimento genérico das ligações por hidrogénio quando os substratos interagem com o enzima.

O encapsulamento do enzima num sistema de micelas invertidas foi conseguido com sucesso. Os resultados demonstraram a capacidade do enzima encapsulado de catalisar reacções de transamidação para

obtenção do ácido acetohidroxâmico com um elevado rendimento de síntese. O efeito de vários parâmetros no sistema de reacção foi também investigado usando um modelo experimental baseado num desenho experimental central compósito e ficou demonstrada a influência do raio micelar na actividade do enzima.

Os resultados obtidos no presente estudo demonstram que a amidase é um enzima com potencialidades de utilização em várias áreas. De facto, a elevada quantidade e qualidade do enzima purificado, as suas propriedades e estabilidade, a formação de agregados com actividade biológica durante a produção, a ampla gama de reacções que é capaz de catalisar e finalmente a imobilização do enzima, permitiram uma visão muito mais clara sobre o potencial deste enzima altamente versátil. Mas para além disto, a detenção de uma metodologia capaz de fornecer conhecimentos e informação sobre os mecanismos responsáveis pela natureza e comportamento do enzima, toma uma importância primordial, pois torna possível projectar e investigar a aplicação deste enzima em qualquer âmbito seja este conhecido ou não.



ENGENHARIA DE SISTEMAS DE POTÊNCIA E AUTOMAÇÃO

Anuário Científico 2005

ISEL

ON THE TRANSIENT MODELLING OF PM MOTORS

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A model for a PM electric motor describing transient operation is presented. The paper provides an outline of the equivalent magnetic circuit modelling method used and the model parameters for a Permanent Magnet motor. The operation of a 40 kW motor-generator is used to illustrate the model accuracy compared with results provided by a conventional analytical model. The advantage of the proposed electric motor model is that it is computationally inexpensive, yet offers high accuracy.

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Conference on
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Modelling and
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SOLVING REAL SCHOOL TIMETABLING PROBLEMS WITH META-HEURISTICS

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School timetabling is a classical combinatorial optimization problem, which consists in assigning lessons to time slots, satisfying a set of constraints of various kinds. Due mostly to the constraints this problem falls in the category of NP-Complete problems. In this paper we try to show an implementation of a decision support system that solves real timetabling problems from various schools in Portugal. This implementation is based on the Simulated Annealing meta-heuristic. The constraints we use were obtained after inquiries made to several schools in Portugal. We show the results on three schools from different levels of teaching.

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Applied Mathematics
and Computer Science,
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Janeiro, Brasil, Abril
2005.*

SCHEDULING OF THERMAL POWER SYSTEMS WITH EMISSION CONSTRAINTS: A MULTIOBJECTIVE APPROACH

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Environmental protection of our habitat in what regards limiting the emission pollution due to thermal power plants burning fossil fuels to convert into electric energy is an emerging issue, giving rise to new constraints regarding emission pollution on thermal plants. Hence, it is necessary to consider these new constraints in the schedule of thermal units. Traditional schedule of thermal units does not include concerns due to emission pollution coming from the operation of power plants. Hence, traditional schedule of thermal units was improved in order to account for emission constraints. Since minimizing the fuel cost and the level of emission are conflicting in nature, a multiobjective approach is used to develop trade-off curves between them. We look not for the optimum solution but for the establishment of compromise solutions, also known by non-inferior or Pareto solutions. The trade-off curves provide important information to the system operator to schedule the units according to emission allowance trading. We present a mathematical formulation for scheduling thermal power systems with emission constraints, modelled as a mixed-integer non-linear constrained optimization problem. The multiobjective approach presented, merging technical and economic knowledge with concerns on emission constraints, is illustrated by a realistic case study with eleven thermal units considering emission pollution.

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CONTROLO DE UM MANIPULADOR ROBÓTICO USANDO VISÃO.

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Este trabalho descreve uma metodologia que permite que um manipulador, equipado com uma câmara de vídeo, se aproxime de um objecto a manipular. A principal característica é que para tal não vamos recorrer a informação de calibração da câmara, o que permite uma grande flexibilidade. O manipulador é controlado unicamente pela informação que retira da imagem, não necessitando inverter a cinemática do sistema. A única restrição é a necessidade de o objecto a capturar estar localizado num plano. Utiliza-se uma rede neuronal na cadeia de controlo, que calcula uma aproximação do jacobiano inverso, não se procedendo, deste modo, à pré-calibração do sistema e não é necessário conhecer as características do manipulador ou do sistema de visão.

INTRODUCTION OF A HUMAN TRANSPORTER IN MUNICIPALITIES: CASE STUDY IN CASCAIS AND OEIRAS

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This paper describes a demonstration project that assesses the introduction impacts of a Human Transporter (HT) in the Cascais and Oeiras municipalities. This introduction of HT's in these municipalities was carried out by some the municipal divisions, namely the Environmental, Transport and Urban Police Departments. The project was carried out, in each municipality, for four weeks to study the energy consumption and the social impact of the HT. The ultimate goal of the present project is to have a global characterization of the possible uses of this EV that will help to introduce governmental legislation about the HT in Portugal.

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Hybrid and Fuel Cell
Electric Vehicle
Symposium
April 2005.*

TRAJECTORY TRACKING CONTROL FOR ELECTRICAL VEHICLES BASED ON DYNAMIC INVERSION AND PASSIVITY

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This paper proposes a trajectory tracking control method for electric vehicles considered as linear parameter varying (LPV) systems containing invertible nonlinear transformation in the output derivatives. The considered model comprises the dynamic models of electric road vehicles (EV) used typically in autonomous navigation and cooperative control. The proposed control structure is especially well suited for EV's and is based on the dynamic inverse of the system and it is completed with an outer stabilizing controller designed by using error feedback and passivity.

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Hybrid and Fuel Cell
Electric Vehicle
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April 2005.*

WIND SPEED PREDICTION USING ARTIFICIAL NEURAL NETWORKS

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In this paper the problem with the introduction of a large quantity of wind generators on the electric grid is presented. A method based in artificial neural networks (ANN) is used to predict the average hourly wind speed. The study starts by choosing the patterns set length to predict de wind speed. The ANN structure and the learning method are chosen as well as the dimensions of the sets of data, training, validation and test. The ANN is tested to archive an acceptable ANN based model. This model is afterwards used to predict the wind speed. The results archived are discussed and the future work perspectives are present.

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WSEAS Transactions
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2005.*

REFERENCE VARIABLES GENERATION USING A FUZZY TRAJECTORY CONTROLLER FOR PM TUBULAR LINEAR SYNCHRONOUS MOTOR DRIVE

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WSEAS International
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The usage of linear permanent-magnet (PM) actuators, and their associated controllers, increases in a wide variety of applications, due to the exhibited high force density, robustness, and accuracy. The s-curve motion profiling is the motion trajectory usually employed in common industrial applications. In this control scheme, the trajectory shape is determined by maximum acceleration, maximum speed, and the target distance. The values of speed and acceleration must be chosen carefully. If they are chosen excessively large or very small, it may not be possible for the system to track the generated trajectory with good accuracy. This paper, considers the control of a single degree-of-freedom (DOF) mechanical system, in which a PM Tubular Linear Synchronous Motor (PM-TLSM) is used as the actuator. Since the fuzzy logic control controllers are based on heuristics are therefore able to incorporate human intuition and experience. The resulting motion trajectory obtained from the fuzzy logic is particularly suited to high accuracy applications such as parallels manipulators, robotics systems and factory automation. Computer simulation results verify the effectiveness of the proposed scheme.

AN ARTIFICIAL NEURAL NETWORK APPROACH FOR DAY-AHEAD ELECTRICITY PRICES FORECASTING

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The deregulation of the electricity markets brings uncertainty to electricity prices. A good forecasting tool provides a risk hedging mechanism for generating companies against daily price volatility. In addition, a generating company can develop an appropriate bidding strategy to maximize its own profit with an accurate next-day price forecast, which represents an advantage facing competition. There are several techniques applied for electricity prices forecasting in the literature. Traditional time series models Auto Regressive Integrated Moving Average (ARIMA) models and simpler Auto Regressive (AR) models have been used for price forecasting. Artificial Neural Networks (ANN) techniques combined with fuzzy logic, which have been mainly used for load forecasting are now used to predict electricity prices. A comparison of neural network and ARIMA models to forecast commodity prices showed the neural network forecasts were considerably more accurate than those of the traditional ARIMA models. This paper is about the use of artificial neural networks on day-ahead electricity prices forecasting. In nowadays-competitive electricity markets, good forecasting tools hedging against daily price volatility are becoming increasingly important. The accuracy and performance of the proposed approach, making use of a three-layered artificial neural network with backpropagation, is evaluated. Results from a real-world case study.

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NEURAL NETWORKS TO ESTABLISH THE STRUCTURAL CONTROLLABILITY AND OBSERVABILITY

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In this paper the usage of neural networks together with bondgraphs allowing the determination of the structural controllability and observability, is presented. The usage of bondgraphs allows a preliminary interpretation that enables the conclusion drawing about the structural characteristics, regardless of the numerical parameters of the system. The artificial neural networks are used to incorporate this knowledge again without the need for a formal mathematical model of the system. A mechanical suspension system is used as a case study.

VEHICLE DRIVETRAIN CUSTOMIZATION FOR TRANSPORTATION FLEETS

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Vehicle Drivetrain Customization goes through the idea that configuration and dimensioning of a vehicle drivetrain can be defined as a function of the drive cycle and the type of service to be developed by the vehicle. In several professional domains, vehicles are used along their life cycle in predefined programmable routine activities.

Having the objective of overpassing some of the technological barriers attained by the introduction of alternative drivetrain technologies, Vehicle Drivetrain Customization is the solution for implementing some objectives to be reached in short-term by road vehicles, like consumptions of less than 2.5 l/100 km.

Several types of alternative fuel and drivetrain are available today, but not all of them are the best suited for a specific application. This work intends to show that the search for an optimized drivetrain for a specific application can reduce energy consumption and pollutant gaseous emission in more than 50%, when compared with general-purpose vehicles.

In spite of general-purpose vehicles present lower acquisition cost, the reductions referred below, in a life-cycle perspective will have economic impact, reducing fuel cost. Other economic benefit can be obtained at a near future, with the perspective set by Kyoto Protocol, where companies will pay for their fleets' pollutant gaseous emissions.

Drivetrain dimensioning, optimization, evaluation and comparison request the use of a simulation tool to test simultaneously the several aspects involved. The validation of the proposed simulation tool used experimental data collected from an urban drive cycle described by a battery electrical minibus in the village of Oeiras, Portugal.

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Vehicle Symposium
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2005.*

ANALOG-DIGITAL VERSUS DSP IMPLEMENTATION OF PARK'S CURRENT CALCULATORS FOR AC MAINS SELF-POWERED SYSTEMS

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This paper presents a comparison between an analog-digital dedicated circuit that evaluates the *Park's* current components on three-phase systems and its counterpart implementation with a DSP. Both circuits operate with the instantaneous active and reactive current component i_d - i_q method. These currents are obtained with a synchronous reference frame which derives from the mains voltage vector. The calculators presented are suitable to perform the direct and inverse current transformations in many self-powered systems connected to the ac mains even at nonideal mains voltage conditions. Laboratorial implementation aspects of the proposed current calculators are shown. Experimental results showing their steady-state performance operation applied to a shunt active filter application are also presented.

IMPROVING ON EXCELLENCE. AN EVOLUTIONARY APPROACH

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In this paper, we present a new hybridization method that, under certain conditions, can be used to improve results obtained by the best existing algorithms for a particular problem. The proposed hybrid uses Evolutionary Algorithm (EA) with a population of algorithms, to simultaneously evolve problem solutions and individual algorithm parameters. As an example of this approach we describe the details of its application to the Job Shop Problem (JSP) and use an EA to enhance results obtained by one of the most successful algorithms for this problem – Nowicki and Smutnicki’s “Taboo Search Algorithm with back jump” (TSAB). The new algorithm not only improved TSAB’s results but also improves best known results for several well known problems.

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OS CERTIFICADOS VERDES: PROMOÇÃO DAS ENERGIAS RENOVÁVEIS NO ESPAÇO IBÉRICO

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Engineering and
Management
Conference”,
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May 2005.*

Sendo o sector eléctrico um dos principais responsáveis pela emissão de gases com efeito de estufa (GEE), torna-se imprescindível promover tecnologias para a mitigação do dióxido de carbono. Neste sentido a energia eléctrica produzida a partir de fontes de energia renováveis (E-FER) poderá apresentar-se como uma opção com vista a mitigar as emissões de GEE. Contudo, a maioria destas fontes de energia não são ainda economicamente viáveis *per se*, não podendo concorrer com as tecnologias convencionais segundo o paradigma de mercado tradicional. Deste modo torna-se indispensável promover a energia eléctrica produzida a partir de fontes de energia renováveis, existindo para isso diversos instrumentos económico-fiscais, sendo o mais recente o mercado de certificados verdes transaccionáveis.

O conceito de certificado verde baseia-se no princípio de que a energia eléctrica produzida a partir de fontes de energia renováveis proporciona dois produtos diferentes ao consumidor de energia eléctrica: um é a própria energia eléctrica, que poderá ser vendida no mercado de energia eléctrica, o outro é um conjunto de benefícios ambientais e sociais que tomam a forma de certificados verdes, os quais poderão ser transaccionados em mercado próprio, gerando assim receitas adicionais à da venda de energia eléctrica para os produtores de E-FER. Neste artigo é realizada a simulação de mercado de certificados verdes de âmbito nacional, para Portugal e Espanha, e de âmbito ibérico, sendo o principal objectivo a avaliação do preço marginal dos certificados verdes de forma a alcançar as quotas de produção de E-FER em 2010, estabelecidas na Directiva 2001/77/CE, que são de 39% para Portugal e de 29,4% para Espanha.

EDUCATIONS ON SCHEDULING HEAD-DEPENDENT HYDRO PLANTS UNDER COMPETITIVE ENERGY MARKET

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As the traditional monopolistic scenery for the electric energy makes way to a competitive energy market, an improved scheduling is crucial for generating companies to face competitiveness. In this new competitive environment, a generating company with hydroelectric facilities faces the optimal trade-off problem of how to make the present profit by the management of the water available for power generation without compromising future potential profit. This problem is known as hydro scheduling. In the short-term, hydro scheduling is concerned with the operation during a time horizon of one to seven days, usually discretized in hourly intervals. The problem is treated as a deterministic one. Where the problem includes stochastic quantities, such as inflows to reservoirs or energy prices, the corresponding forecasts are used. Modern computers make linear network programming algorithms widely used for hydro scheduling. These algorithms accommodate easily constraints such as the water balance equation and hydro plants limits of operation. In addition, linear network programming algorithms lead to extremely efficient codes, which are commercially available. Head-dependent hydro plants, due to a non-linear power generation function of water discharge and head, are not properly modelled by linear methods. In this paper we present an educational approach of conceptually teaching the hydro scheduling problem in light of market conditions. The approach is based on a computer support and is illustrated by a case study, designed for teaching power engineers in this indubitably important issue to achieve a superiority judgment in head-dependent hydro plants.

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NONLINEAR APPROACH FOR SHORT-TERM SCHEDULING OF A HEAD-SENSITIVE HYDRO CHAIN

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June 27-30, 2005.*

This paper is on the problem of short-term hydroscheduling, particularly concerning a head-sensitive hydro chain. In a competitive electricity market, generation companies have to maximize their profits selecting the best strategy. We propose a method based on nonlinear programming that considers power generation a function of water discharge and also of the head. The proposed method provides a higher profit for the company in comparison with classical optimization methods based on linear programming that ignores head dependence. The proposed non-linear approach allows considering the non-linear relationship between the power generation, the water discharge and the head. Numerical testing results show that the algorithm is computationally adequate to the STHS problem for hydro chains with run-of-the-river hydro plants, because the head effect has to be considered for improving the producibility. Even in sceneries with low natural inflows the NLP approach achieves a higher average storage than the LP approach as shown in the case study, due to the consideration of the head change effect, thereby yielding larger profits for the hydro generation company.

EMISSIONS TRADING IMPACT ON THE POWER INDUSTRY WITH APPLICATION TO THE IBERIAN ELECTRICITY MARKET

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The Kyoto Protocol establishes a legally binding obligation for industrialized countries to reduce their emissions of greenhouse gases (GHG). In aggregate, emissions are to be reduced by at least 5% below 1990 levels by 2008-2012. In accordance with article 4 of the Kyoto Protocol, the European Community is committed to reduce the aggregate anthropogenic emissions of GHG by 8%, compared to 1990 levels, in the period 2008-2012, with different targets set among Member States (Portugal with a maximum increase of 27% and Spain with a maximum increase of 15%).

The purpose of this paper is to evaluate not only the impact of GHG emissions trading on the Iberian Electricity Market (IBELM) power industry, but also the likelihood for the reduction in the electricity sector emissions. A SIMulator for Electricity and Carbon markets (SIMEC) was developed for that purpose. Given the system power plants characteristics, demand data and CO₂ allowance prices; SIMEC computes the electricity market clearing price, power generation by technology, CO₂ emissions and power industry profits. A rise in electricity prices is expected when CO₂ constraints are in place with a sharp increase in off-peak hours, when normally coal power plants clear the market. Increases in electricity prices are evaluated for different scenarios of allowance prices. Producers that do not face carbon liabilities or facing less carbon liabilities than the market clearing technology will have a positive effect on profits.

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A CONTRIBUTION FOR TEACHING ON INDUSTRIAL FIELDBUSES

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16th EAEEIE
Conference
Lappeenranta,
Junho 2005.*

Fast changing technologies, while being of great importance for future engineers, are often a challenge for teaching, both in curricular and logistic aspects. Fieldbus systems are part of the competencies of EIE engineers that deserve special investment at the university curricula and laboratories due to their diversity, permanent and fast evolution, and essential role in modern industrial automation and control practice. This paper presents a discussion of curricula and resources that have been implemented at ISEL in order to achieve the required competencies in fieldbuses by electrical engineers. Historical facts and actual trends are at the starting point for discussion, leading to the proposed methodological issues on both theoretical and experimental teaching.

REMOTE ALARM AND COMMAND SYSTEM FOR RESIDENTIAL DOMOTICS THROUGH GSM – SMS

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The conception of an electronic system for alarm monitoring and remote command devices, through GSM mobile net using short messages (SMS) is described.

It was developed as a low cost solution based on a common mobile phone and an Intel 8751 microcontroller. A prototype was built with a versatile configuration for residential domotics, including 6 binary inputs and 6 binary outputs, allowing to be associated to 4 different users (mobiles phones). The main characteristics of the hardware and protocol used for communication are described. The system was conceived in order to get an adequate performance, which came to be confirmed with the prototype. Reference is also made to other known systems for similar functions.

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Electrotécnica,
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DSP SLIDING-MODE CONTROLLERS FOR THREE-PHASE FOUR-WIRE CONVERTERS WITH SPLIT DC LINK CAPACITOR

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This paper presents the voltage regulation system design for a three-phase four-wire voltage converter using sliding-mode control techniques. Two regulation systems proposed are applied to a three-leg voltage source converter with split dc link capacitor connected to the ac mains. System modelling and controllers syntheses with digital implementation are realized. Experimental results highlight the voltage regulation characteristics in terms of steady-state and transient responses. The robustness to disturbances influence is also analysed. Conclusions are taken with respect to the different approaches presented and the type of application where the dc voltage regulation is needed, like active power filters, unified power flow controllers, neutral current compensators, pwm rectifiers and others.

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IEEE Power Electronics
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Brasil, Junho, 2005.

LINEAR AND SLIDING-MODE CONTROLLERS FOR THREE-PHASE FOUR-WIRE POWER CONVERTERS

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Voltage regulation systems play an important role in all self-powered systems connected to the ac mains, like active filters, unified power flow controllers, advanced static VAR compensators, PWM rectifiers, uninterruptible power supplies and neutral current compensators. In these systems the voltage regulation it is absolutely necessary to the operation of the voltage source converters in order to sink or feed current into mains.

Some works have been realized in the design of voltage regulators for three-phase four-wire converters. An insight study of the voltage regulation system using a linear controller was already done, but less attention has been paid to sliding-mode controllers for power converters with neutral current control.

This paper presents the voltage regulation system design for a three-phase four-wire voltage converter using linear and sliding-mode control techniques. The regulation systems proposed are applied to a four-leg voltage source converter connected to the ac mains. System modelling and controllers syntheses are realized and compared. Digital simulations highlight the voltage regulation characteristics in terms of steady-state and transient responses. The robustness to disturbances influence is also analysed. Conclusions are taken with respect to the different approaches presented and the type of application where the dc voltage regulation is needed.

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IEEE-IES International
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MULTIOBJECTIVE OPTIMISATION APPROACH FOR UNIT COMMITMENT UNDER EMISSION ALLOWANCE TRADING

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Junho a 2 de Julho de
2005.*

As a consequence of growing environmental concern worldwide the impact of conventional power plants on the environment must be considered, reducing emissions of greenhouse gases. Directive 2003/87/EC of the European Parliament and of the Council of 13 October 2003 establishes the scheme for greenhouse gas emission allowance trading within the Community. Russia's approval on November 2004 to rectify the Protocol of Kyoto, an international and legally binding agreement to reduce greenhouse gases emissions worldwide, closed a long period of uncertainty, therefore allowing Quioto entry into force in 2005. Environmental protection of our habitat in what regards limiting the pollutant emissions due to thermal power plants is an emerging issue, giving rise to new constraints regarding pollutant emissions on thermal plants. Some research work has already been done, particularly concerning the economic dispatch problem. We present a mathematical formulation for the unit commitment problem modelled as a large-scale, dynamic, mixed-integer non-linear programming problem. Finally, we present a case study for a schedule of thermal units with a period of 1 hour and a time horizon of 168 hours, considering pollutant emissions. The trade-off curve between fuel cost and pollutant emissions, in a way to provide important information to the system operator to schedule the units according to emission allowance trading, is obtained.

UTILIZAÇÃO DE MODERNAS TECNOLOGIAS NO ENSINO EXPERIMENTAL DE ACCIONAMENTOS ELECTROMECHANICOS.

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As tecnologias de semicondutores possibilitaram o aparecimento de dispositivos de potência e de sinal destinados à construção compacta de onduladores de tensão trifásicos, especialmente vocacionados para a indústria dos accionamentos com máquinas de corrente alternada. Todo o circuito electrónico de potência, baseado em IGBT, reside num único módulo híbrido compacto. O sistema completo de guiamento (*driver*) e de auto-protecção dos semicondutores de potência de um ondulador trifásico em ponte, existe também num único circuito integrado, já adaptado aos altos desníveis de tensão entre os andares de guiamento. Para o projecto e implementação esses dispositivos são associados, constituindo conjuntos compactos e com boas características de robustez. Em alternativa, este tipo de agrupamento também já é disponibilizado por alguns fabricantes, que produzem associações rectificador-ondulador-*chopper-driver*, com os módulos dos tipos acima referidos já montados em placas de tecnologia *Surface Mounted Devices* (SMD), e contendo condensadores intermédios, auto alimentação e várias protecções. Esta tecnologia, vem simplificar enormemente a construção deste tipo de conversores estáticos. Impondo algumas condições na parte de comando, demonstra-se que os mesmos produtos permitem ainda realizar outras topologias de conversores, o que é de grande interesse para fins didácticos e para trabalhos de investigação. Neste artigo comentam-se as características, potencialidades e exigências destas novas soluções. Fazem-se considerações e sugestões de projecto de onduladores e de conversores de contínua para contínua (*choppers*). Por fim apresentam-se resultados experimentais de ensaios efectuados em protótipos laboratoriais utilizados no ensino.

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DOUBLY FED INDUCTION GENERATOR SYSTEMS FOR VARIABLE SPEED WIND TURBINE

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This paper presents results of a study concerning the dynamic behaviour of a wind energy system powered by a doubly fed induction generator with the rotor connected to the electric network through an AC-AC converter.

A tendency to put up more and more wind turbines can be observed all over the world. Also, there is awareness in taking into account the requirements of a clean environment, due to the need to preserve our habitat. Renewable energy sources not contributing to the enhanced greenhouse effect, specially wind power, are becoming an important component of the total generation. Hence, research concerning the dynamic behaviour of wind energy systems is important to achieve a better knowledge.

Wind energy continues to move forward in Europe and deregulation provides an opportunity for investments in WECS. Hence, it is expected that wind power will be a significant component of the total generation mix in the near future. Due to the advances in power electronics it is possible to use the doubly fed induction generator system with variable speed connected to the electrical network through an AC-AC converter, improving the efficiency of the power conversion.

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ALL SILICON MARX-BANK TOPOLOGY FOR HIGH-VOLTAGE, HIGH-FREQUENCY RECTANGULAR PULSES

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This paper discusses the operation of a fully integrated solid-state Marx generator circuit, which has been developed for high-frequency (kHz), high-voltage (kV) applications needing rectangular pulses. The conventional Marx generator, used for high-voltage pulsed applications, uses inductors, or resistors, to supply the charging capacitors voltage, which has the disadvantages of size, power loss and frequency limitation. The proposed circuit takes advantage of the intensive use of power semiconductor switches, replacing the passive elements in the conventional circuit, to increase the performance of the classical circuit, strongly reducing losses and increasing the pulse repetition frequency. Also, the proposed topology enables the use of typical half-bridge semiconductor structures while ensuring that the maximum voltage blocked by the semiconductors is the voltage of each capacitor (i.e. the power supply voltage), even when the switching is not synchronized, and in fault conditions. A laboratory prototype with five stages, 5 kW peak power, of this all silicon Marx generator circuit, was constructed using 1200 V IGBTs and diodes, operating with 1000 V d-c input voltage and 10 kHz frequency, giving 5 kV pulses, with 10 μ s width and 50 ns rise time.

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GERADOR ASSÍNCRONO AUTO-EXCITADO CONTROLADO POR PROCESSADOR DIGITAL DE SINAL.

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2005.*

Este artigo apresenta a implementação de uma estratégia global de controlo de um gerador assíncrono trifásico auto-excitado por ondulator de tensão trifásico controlado em corrente, de modo a esta-belecer as correntes de excitação e de carga apropriadas ao funcionamento da máquina. A técnica utilizada para controlo da máquina é a de orientação de campo. A tensão do lado *DC* do ondulator é mantida constante através de um anel de controlo implementado com um controlador do tipo *PI*, com robustez relativamente à variação dos valores de carga e da velocidade de accionamento. O desempenho do sistema é ilustrado com resultados experimentais.

DESIGN OF LOW-VOLTAGE LOW-POWER PIPELINE ADCS USING A SINGLE-PHASE SCHEME

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The application of a single-phase scheme to low-voltage pipeline ADCs designed in standard CMOS technologies is described. The referred technique explores the gap between the high conductance region of PMOS and NMOS switches at low power-supply voltages and the fast clock transitions that exist in advanced CMOS technologies. In order to validate the theoretical findings and assess the performance of the proposed technique, a 10-bit 4 MS/s pipeline ADC was fully designed and simulated, first with all switches driven by a conventional six-phase clock generator, and after with only a single-phase scheme. Simulated results show the signal integrity and overall performance are preserved, pointing to the use of simpler low-voltage circuits and avoiding the complexity as well as the problems normally created by the use of non-overlapping clock generators.

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BRUSHLESS DC MOTOR: POSITION LINEAR CONTROL SIMULATION

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The Brushless Direct Current (BLDC) motor is one of the motors types rapidly gaining attractiveness. Actually they are becoming widely used in various consumer and industrial systems. As the name implies, BLDC motors do not use brushes for commutation, they are electronically commutated. This paper presents a Matlab simulation model that includes the control speed and position of a trapezoidal back-emf BLDC motor. The model consists of position and speed linear controllers, reference current generation, current controller and a three phase voltage inverter. Most of the applications now use a Pulse Width Modulation (PWM) current controller. The solution here proposed is new because it uses a hysteretic vectorial control in $\alpha\beta$ to control the current.

EXPERIMENTAL VALIDATION OF PHOTOVOLTAIC CELLS MODELS

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Beginning with the definition of photovoltaic cells as semiconductor devices that allow making the conversion of luminous energy in electric energy, the different types of cells are characterized in a brief manner, in accordance with the type of used silicon:

- Monocrystalline silicon, the most used material, covering about 60% of market, presenting an efficiency about 15%;
- Polycrystalline silicon, with a market quote about 30% and an efficiency about 12%;
- Amorphous silicium, representing about 4% of market, and efficiency in the order of 6%.

With the accomplished tests it is intended to reach the following objectives:

- Obtain the voltage-current characteristic curves;
- Determination of the open-circuit voltage variation, V_{ca} , and short circuit current variation, I_{cc} , with temperature and with incident radiation intensity;
- Attainment of ideal inclination angle, in accordance with the radiation intensity received in one given time of the year;
- Verification of the relationship between maximum power, incident radiation and temperature.

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POWER GENERATION EFFICIENCY IMPROVEMENT IN CASCADED AND HEAD-DEPENDENT RESERVOIRS

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This paper is on the problem of short-term hydro scheduling (STHS), particularly concerning cascaded and head-dependent reservoirs. We propose an efficient method, based on nonlinear programming (NLP), for power generation efficiency improvement. This method considers hydroelectric power generation as a function of water discharge and also of the head. The proposed method provides higher profit for the generating company (GENCO), at a negligible extra computational effort, in comparison with classical optimisation methods based on linear programming (LP) that ignore head dependence. The new environment of competitive electricity markets for energy requires new computing tools to allow generating companies to achieve improvement on power generation efficiency, which is crucial to face competitiveness. A generating company should not ignore the head change effect for cascaded and head dependent reservoirs in order to improve power generation efficiency. This effect implies not only a nonlinear dependence between the power generation, the water discharge and the head, but also implies that the maximum water discharge, giving the maximum power generation, is a function of the head. This paper proposes a nonlinear model for cascaded and head dependent reservoirs in order to consider the head change effect. This model has been successfully tested on a realistic case study by comparing the nonlinear programming results with linear programming results.

UNIT COMMITMENT WITH ENVIRONMENTAL CONSIDERATIONS: A PRACTICAL APPROACH

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This paper provides a practical approach to the unit commitment problem designed to simultaneously address the economic issue of the fuel costs incurred on the commitment of the units and the environmental considerations due to emission allowance trading. A simultaneously address of fuel costs with the emission implies the consideration of a multiobjective unit commitment emission problem. A trade-off between fuel cost and the emission in a way to aid decision-makers concerning emission allowance trading is obtained, due to this practical approach.

A compromise between the fuel costs incurred on the commitment of the units with the level of emission implies the consideration of a multiobjective problem for supporting the decision maker. The decision maker can choose an appropriated commitment for the units with the help of the trade-off curves and taking into consideration the emission allowance trading. In the best emission commitment, thermal units with higher levels of emission are committed at a lower level of output, in comparison with the best cost commitment. Hence, more units have to be committed to satisfy the same demand, incurring in higher fuel costs and operating thermal units at lower efficiency points, implying an increase on the total cost for the best emission commitment. The results show that the proposed approach is efficient for obtaining the schedule and the trade-off curves with a small CPU-time requirement.

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SPOT PRICE SIMULATION AND VOLATILITY ANALYSIS IN THE FUTURE IBERIAN ELECTRICITY MARKET

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Unlike other commodities, electricity lacks of relevant storage mechanisms (with the exception of pumped storage hydro plants) which implies the need for a continuous balancing of demand and supply. On the other hand, in the short run, demand is very rigid in respect to price.

As a result, electricity prices can change drastically compared to the prices of other commodities or equities, leading to an electricity price volatility consistently and significantly higher than other products.

Therefore, price volatility is a major issue in liberalized electricity markets as far as risk management is concerned.

In this paper we evaluate the impact of the Portuguese and Spanish electricity markets integration on the day ahead market price volatility. For that purpose we develop an adaptive conjectural variations model which is implemented in GAMS language. We estimate the degree of competition in the Spanish pool using an iterative secant method applied to a conjectural variations oligopoly model. Using the estimate obtained, we simulate the Portuguese and Spanish markets in autarky and the integrated market, known as the Iberian Electricity Market (IBELM).

We found strong evidence that IBELM will promote price stability both from the Portuguese and Spanish markets point of view, leading to a less risky market for Iberian power producers and consumers.

QUADRATIC OPTIMIZATION FOR A HEAD-DEPENDENT HYDRO CHAIN

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A natural approach to short-term hydro scheduling is to model the system as a network flow model, because of the underlying network structure subjacent in hydro chains. This network flow model is often programmed as a linear one. Linear programming is a well-known optimization method and standard software is available. However, linear programming typically considers that power generation is linearly dependent on water discharge, thus ignoring head dependence. Also, mixed-integer linear programming is becoming frequently used for hydro scheduling [6-7], where binary variables allow modeling of start-up costs to avoid unnecessary start-ups, and of discrete hydro unit-commitment constraints. However, the discretization of the non-linear dependence between power generation, water discharge and head, used in mixed-integer linear programming to model head variations, augment the computational burden required to solve this problem. A nonlinear model has advantages compared with a linear one. A nonlinear model expresses the hydropower generation characteristic more accurately, taking into account the head change effect [2,8]. Particularly, quadratic optimization compromises one of the most important areas of nonlinear programming. In this paper, we use a quadratic optimization method to solve the short-term hydro scheduling problem. We report our experience with the proposed quadratic optimization method on a hydro chain based on a realistic hydro system with three cascaded reservoirs, considering a time horizon of 168 hours. As a new contribution to earlier studies, mainly for medium and long-term planning procedures and ignoring head dependence, we address the short-term behavior of head-dependent reservoirs in a hydro chain.

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SIMULATION OF A DOUBLY FED INDUCTION GENERATOR SYSTEM WITH A VARIABLE SPEED WIND TURBINE

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This paper presents a study concerning the simulation of the association of a doubly fed induction generator system with a variable speed wind turbine. While the stator of the doubly fed induction generator is directly connected to the electric network the rotor is connected to the electric network through an AC-AC converter in this association. A trend to allocate more and more wind turbines can be observed all over the world. Also, there is a trend to take into account the requirements of a clean environment, due to the need to preserve a healthy habitat. Consequently, wind power mills are suitable for electric energy generation in power systems and variable speed wind turbine equipped with doubly fed induction generator is in nowadays one of the most capable configurations for wind energy conversion. Deregulation provides an opportunity for investments in WECS. Hence, it is expected that wind power will be a significant component of the total generation in the near future. Advances in power electronics made possible to use the doubly fed induction generator system with variable speed wind turbines connected to the electrical network through an AC-AC converter, at a lower cost and improving the conversion efficiency. This paper is a contribution to the study of doubly fed induction generator system with variable speed wind turbines. This type of equipped WECS is in nowadays one of the most capable configurations for wind energy conversion. Hence, research concerning the behavior of this type of WECS is important to achieve a better knowledge of the system.

ANN APPROACH TO WECS POWER FORECAST

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In this work-in-progress the problem with the future integration of large quantity of wind generators in the Portuguese electric grid is presented. A method based in artificial neural networks (ANN) is used to predict the average hourly wind speed. The work starts by choosing the patterns set length, the ANN structure and the learning method. As well as the dimensions of the data sets, training, validation and test. The ANN is tested with several structures until it archives an acceptable ANN based model. The obtained model is used to predict the wind speed and to forecast the power produced. The results archived are discussed. The future work perspectives are present.

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IMPACT OF REGIONAL ELECTRICITY MARKETS INTEGRATION ON POOL PRICES: AN APPLICATION TO THE IBERIAN ELECTRICITY MARKET

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Universities Power
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In this paper we evaluate the impact of regional electricity markets integration on the day ahead pool prices. For that purpose we implement a conjectural variations model with simulations carried out using GAMS simulation tool. For different competitive regimes, ranging from perfect competition to collusive arrangements, we simulate the Portuguese and Spanish markets in autarky and integrated in the Iberian Electricity Market (IBELM).

It is shown that for competitive regimes close to the perfect competition paradigm the integration leads to a price in between the autarky prices. In regard to the simulations of IBELM in perfect competition it is concluded that the integration promotes a strong reduction in price for Portugal and a small increase for Spain.

Moreover, the mitigation of market power emerges as the major determinant for increased market power conjectures. In this case, the simulations carried out for the IBELM show that the integration promotes a decrease in prices for both the Portuguese and the Spanish markets, since power producers with a significant market power in autarky markets compete with producers from the other market.

In conclusion, it can be stated that market integration is an efficient policy to enhance market performance as far as market power is concerned, with a very limited regulatory intervention, and a way to promote efficient transactions between producers and consumer of different markets when relevant supply/demand asymmetries between the two markets are presented.

VEHICLE DRIVETRAIN CUSTOMIZATION: APPLICATION TO A POSTAL SERVICE FLEET

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Current automotive manufacturers' strategy is to design more modular vehicles in order to increase the vehicle customization. This customization has been focused in the interior layout and chassis configuration, but the extension of this perspective to drivetrain configuration can provide great benefits, especially at professional domains, where routine activities are kept along vehicle life cycle. This paper intends to illustrate the energy and environmental benefits of drivetrain customization for a collection and distribution drive cycle of a Postal services company.

A methodology following four main steps (Service and drive cycle characterization, Minimal performance requirements definition, Drivetrain dimensioning and Performance Comparison) was used with the goal of the vehicle drivetrain customization.

Dimensioning, optimization, evaluation and comparison of alternative vehicle drivetrain requested the use of a simulation tool to test simultaneously the several aspects involved. Simulation tool validation was based on the experimental data collected from diesel and battery operated electrical small vans.

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MODERN TECHNOLOGIES FOR EXPERIMENTAL EDUCATION IN INDUSTRIAL ELECTRONICS AND ELECTRIC DRIVES

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This paper describes the methods used by the teaching group of power electronics and electrical drives of Electrical Engineering and Automation Department of Instituto Superior de Engenharia de Lisboa (Portugal) to increase the effectiveness of experimental training in the areas of industrial electronics and electric drives. It is well known that the interest of new students for electrical engineering courses has decreased, all over the world, and some proactive actions have to be done by engineering schools in order to increase their attractiveness. The approaches followed by this teaching group were intended to improve the student enrolment and to develop sustained competences in the electrical engineer profile by a fair balance between didactic tools and industrial equipment. A judicious introduction of industrial material in laboratory work can be both stimulating as well as a valuable link to the real world. The versatility and moderate cost of modern integrated power electronics modules, the capacities of modelling and control dedicated software, the new generation of digital signal processors and also the judicious use of more complex industrial equipment, allow new experimental training challenges. This set of equipment allows building a variety of configurable open systems, with more or less complexity, that can be explored at different levels of power electronics and electrical drives, from the power stage to the control functions.

HIGH-VOLTAGE HIGH-FREQUENCY MARX-BANK TYPE PULSE GENERATOR USING INTEGRATED POWER SEMICONDUCTOR HALF-BRIDGES

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This paper discusses the operation of an all silicon-based solution for the conventional Marx generator circuit, which has been developed for high-frequency (kHz), high-voltage (kV) applications needing rectangular pulses. The conventional Marx generator, for high-voltage pulsed applications, uses passive power components (inductors or resistors), to supply the energy storage capacitors. This solution has the disadvantages of cost, size, power losses and limited frequency operation. In the proposed circuit, the bulky passive power elements are replaced by power semiconductor switches, increasing the performance of the classical circuit, strongly reducing costs, losses and increasing the pulse repetition frequency. Also, the proposed topology enables the use of typical half-bridge semiconductor structures, and ensures that the maximum voltage blocked by the semiconductors equals the power supply voltage (i.e. the voltage of each capacitor), even with mismatches in the synchronized switching, and in fault conditions. A laboratory prototype with five stages, 5 kW peak power, of the proposed silicon-based Marx generator circuit, was constructed using 1200 V IGBTs and diodes, operating with 1000 V d-c input voltage and 10 kHz frequency, giving 5 kV/1 A pulses, with 10 μ s width and 50 ns rise time.

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SCHEDULING OF HEAD-SENSITIVE HYDRO PLANTS UNDER PROFIT-BASED ENVIRONMENT FOR POWER ENGINEERING EDUCATION

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International
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Distance Learning and
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This paper presents an educational approach for teaching on the optimal management of the water available in hydro plants to convert into electric energy, combining management knowledge of head-sensitive hydro plants with computer simulation methods based on linear and non-linear network programming, on the assessment of accurate short-term decisions for the hydroelectric energy, article of trade, under profit-based environment. The optimal scheduling of the hydroelectric facilities available is essential for generating companies to face competitiveness. Moreover, also responds to climate change contributing to reduce fossil fuels energy dependency. Hence, presenting concerns on the optimal exploitation of hydro resources for undergraduate power engineering education is important for preparing the future engineers to address the problem on nowadays-competitive energy market. In a competitive energy market, generation companies have to maximize their profits selecting the best strategy. The schedule is formulated as an optimal trade-off problem of how to make the present profit by the management of the water available for power generation without compromising future potential profit.

MODERN TECHNOLOGIES APPLIED IN EXPERIMENTAL EDUCATION ON ELECTRICAL DRIVES EXAMPLE: PWM COMMAND FOR THE THREE-PHASE VOLTAGE-SOURCE INVERTER

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This paper describes the methods used by the teaching group of power electronics and electrical drives of Electrical Engineering and Automation Department of Instituto Superior de Engenharia de Lisboa (Portugal) to increase the effectiveness of experimental training in the areas of industrial electronics and electric drives. The approaches followed by this teaching group were intended to improve student enrolment and to develop sustainable competences in the electrical engineer profile. The solution consists of finding the most up to date material, essentially from industry, in order to create powerful lab training tools in a stimulating environment. The versatility and moderate cost of modern integrated power electronics modules, the capacities of modelling and control dedicated software, the new generation of digital signal processors and, finally, the judicious introduction of more complex industrial equipment, open new experimental training challenges. The set of equipment actually available allows building a variety of configurable open systems, with more or less complexity that can be explored at different levels of power electronics and electrical drives, from the power stage to the control functions. After detailing the above policy, and discussing the opportunities brought by new technologies, the paper focus on a particular example, demonstrating how easy can be the implementation of an AC motor drive experiment with this modern approach.

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Conference on
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October 2005.*

UNIFIED POWER FLOW CONTROLLERS WITHOUT DC BUS: DESIGNING CONTROLLERS FOR THE MATRIX CONVERTER SOLUTION

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This paper synthesizes active and reactive power controllers for matrix converters operating as Unified Power Flow Controllers (UPFC) in Flexible AC Transmission Systems (FACTS). Since matrix converters need no DC link, the resulting UPFC has reduced volume and cost, together with higher reliability. An UPFC model is proposed and used to obtain both power controllers and a modified Venturini PWM modulation is adopted for the matrix converter. Simulations results are presented and discussed.

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International
Conference on
Electrical Engineering
(CEE'05), Coimbra,
October 2005.*

SUSTAINABLE MOBILITY: PART I - MAIN PROBLEMS

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The sustainable mobility is the object of two papers being this paper the first part. The purpose of the two papers is to present the mobility needs and problems of our societies, from the energy, oil dependency and environment point of view (Part I) and to present some of the actual and future solutions provided by electric and hybrid vehicles, as well as by other mobility solutions (Part II). The main challenges to a greater penetration of the electric and hybrid vehicles are also discussed.

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SUSTAINABLE MOBILITY: PART II - SOME POSSIBLE SOLUTIONS USING ELECTRIC AND HYBRID VEHICLES

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This paper is the second of two. The purpose of the two papers is to present the mobility needs and problems of our societies, from the energy, oil dependency and environment point of view (Part I) and to present some of the actual and future solutions provided by electric and hybrid vehicles, as well as by other mobility solutions (Part II). The main challenges to a greater penetration of the electric and hybrid vehicles are also discussed.

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CONTROLO AUTOMÁTICO DE UM ACELERADOR VAN DE GRAAFF

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O ITN (Instituto Tecnológico e Nuclear) está empenhado em automatizar os procedimentos de operação do acelerador Van de Graaff, aí colocado, para realizar as experiências de RBS, Canalização iónica, PIXE e Microsonda. Actualmente, o ajuste das inúmeras variáveis que determinam o seu funcionamento é realizado manualmente por um pequeno grupo especializado de pessoas. Com este trabalho pretende colocar-se o comando e controlo do acelerador num computador pessoal, através de uma placa de aquisição de dados, de modo a facilitar a sua operação. Sendo necessário, porém, traduzir em algoritmos, implementados por hardware e software, toda a complexa operação desta máquina.

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SUPERVISÃO E CONTROLO DE UMA EVAPORADORA DE ALTO VAZIO

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Neste trabalho desenvolve-se um sistema para monitorizar e controlar o funcionamento de experiências conduzidas na evaporadora de ultra-alto-vazio, do CFNUL. Esta máquina é especialmente vocacionada para recozimentos de amostras a alta temperatura, com controlo e medição de temperatura, e evaporação de materiais por canhão de electrões para deposição de filmes finos com controlo de espessura, dentro de pressões absolutas muito baixas, inferiores a 10^{-10} mbar. Com base numa placa de aquisição de dados vai desenvolver-se um sinóptico num PC para supervisionar o funcionamento da evaporadora e controlar automaticamente todas as funções a partir do PC.

MODERNIZAÇÃO DO EQUIPAMENTO DO LABORATÓRIO DE HIPERFINAS DO CFNUL PARA CORRELAÇÕES ANGULARES PERTURBADAS

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No laboratório de Hiperfinas do CFNUL procede-se à modernização do hardware associado aos detectores de radiação e aos fornos tubulares para experiências “in situ” de Correlações Angulares Perturbadas, PAC, até $1000^{\circ}\text{C}\pm 10^{\circ}\text{C}$. Deste modo, desenvolvem-se novas bases transistorizadas para os fotomultiplicadores, PM's, optimizadas para elevadas taxas de contagens e baixo consumo, com melhor linearidade e redução do ruído. Os fornos, alimentados a partir duma topologia com controlo de corrente para minimizar as variações de temperatura, utilizam dupla blindagem térmica para reduzir as perdas de calor para o exterior e a espessura das paredes para as experiências de PAC.

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Actas da Conferência Nacional de Física 2005, Porto, 2 e 3 de Dezembro, 2005.

FILTROS ACTIVOS DE POTÊNCIA - METODOLOGIAS DE CONTROLO E IMPLEMENTAÇÃO DIGITAL

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2005*

Actualmente verifica-se uma proliferação de cargas não lineares baseadas em conversores estáticos de potência. Estas cargas geram uma quantidade considerável de harmónicas de corrente na rede de energia eléctrica. As harmónicas são responsáveis pela ocorrência de inúmeros fenómenos indesejáveis na rede podendo distorcer consideravelmente as tensões levando à redução da qualidade de energia eléctrica.

Na rede de energia verificam-se alterações constantes de topologia. O conteúdo harmónico exhibe ainda um carácter aleatório. Nestas circunstâncias as soluções convencionais baseadas em filtros passivos revelam-se, em algumas situações, ineficazes na compensação das correntes de fase e neutro. Este trabalho pretende dar um contributo para a melhoria da qualidade de energia eléctrica em redes trifásicas de neutro distribuído através da implementação de um sistema dinâmico de compensação harmónica designado por “Filtro Activo de Potência”.

Propõe-se um método de controlo e estruturas de compensação capazes de compensar diversos parâmetros na rede de energia eléctrica. Realiza-se o estudo, a modelação e a simulação dos sistemas constituintes do filtro activo de potência. São apresentados os aspectos referentes à sua implementação laboratorial num sistema de processamento digital de sinal. Os resultados experimentais comprovam a validade dos modelos utilizados e a correcta operação deste sistema de compensação harmónica.

INTEGRAÇÃO DE MERCADOS LIBERALIZADOS DE ENERGIA ELÉCTRICA COM APLICAÇÕES AO MIBEL

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A criação do Mercado Ibérico da Electricidade (MIBEL) constituirá um marco na construção do Mercado Interno da Energia e permitirá acelerar o processo de aplicação das disposições da Directiva 2003/54/CE, uma vez que favorece a concorrência entre as empresas do sector, deverá beneficiar os consumidores dos dois países e permitirá o acesso ao mercado a todos os participantes em condições de igualdade, transparência e objectividade.

Com vista ao estudo do impacto da integração de mercados liberalizados de energia eléctrica a presente dissertação apresenta abordagens teóricas e aplicações ao MIBEL. Para tal é dado especial enfoque a dois determinantes fundamentais na integração de mercados. Por um lado mitigação do poder de mercado como resultado do incremento da competição entre as empresas produtoras de energia eléctrica e, por outro lado, o aumento de eficiência económica resultante das assimetrias de custos de produção e procura verificada nos dois mercados.

As aplicações ao MIBEL são efectuadas com base na implementação de um modelo de variações conjecturais que se apresenta especialmente adequado à representação de diversos níveis de intensidade competitiva do mercado. O equilíbrio de mercado é determinado numericamente com recurso ao pacote de simulação GAMS.

Os resultados obtidos evidenciam o impacto relativo de cada um dos determinantes estudados em relação aos preços de mercado, quantidade produzida, consumida e exportada, lucro dos produtores, excedente dos consumidores e bem estar social.

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*Dissertação de
Doutoramento, FEUNL,
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AUTOMATIZAÇÃO DA REALIZAÇÃO DE HORÁRIOS EM ESCOLAS PORTUGUESAS

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Doutoramento em
Engenharia
Electrotécnica e de
Computadores realiza-
do no Instituto
Superior Técnico em
Dezembro de 2005*

Este trabalho teve como objectivo resolver o problema da elaboração automática de horários de instituições dos diferentes regimes de ensino de Portugal tendo em conta o compromisso qualidade vs. tempo. Definiu-se um modelo adaptável para as diferentes escolas. Trabalhou-se com dados recolhidos de 62 escolas de Portugal. Enquadrou-se este problema no domínio mais vasto dos problemas de optimização combinatório. Definiu-se uma função de custo adequada ao problema e mostrou-se um modo eficiente de a calcular. Aplicaram-se algumas das técnicas heurísticas e meta-heurísticas mais comuns para a resolução deste tipo de problemas. Tendo em conta a enorme dimensão do espaço de pesquisa deste problema e do modo eficiente de calcular a função de custo introduziram-se dois operadores de vizinhança, comparando-se os resultados obtidos entre eles. Apresentou-se uma medida da eficiência do algoritmo. Apresentaram-se resultados comparativos de três escolas típicas dos diferentes regimes de ensino. Mostrou-se o ganho de qualidade e de eficiência que se obtém com este sistema.



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FÍSICA

Anuário Científico 2005

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MORPHOLOGICAL AND STRUCTURAL CHARACTERIZATION OF $\text{CrO}_2/\text{Cr}_2\text{O}_3$ FILMS GROWN BY LASER-CVD

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This work reports on the synthesis of chromium (III, IV) oxides films by KrF laser-assisted CVD. Films were deposited onto sapphire substrates at room temperature by photodissociation of $\text{Cr}(\text{CO})_6$ in dynamic atmospheres containing oxygen and argon. A study of the processing parameters has shown that partial pressure ratio of O_2 to $\text{Cr}(\text{CO})_6$ and laser fluence are the prominent parameters that have to be accurately controlled in order to co-deposit both crystalline oxide phases. Films consistent with such a two-phase system were synthesised for a laser fluence of 75 mJ cm^{-2} and a partial pressure ratio about 1.

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Applied Surface Science, 147 (2005) 423.

MEASUREMENTS OF NEW PHYSICS IN B \rightarrow $\pi\pi$ DECAYS?

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If new physics (NP) is present in $B \rightarrow \pi\pi$ decays, it can affect the isospin $I=2$ or $I=0$ channels. In this paper, we discuss various methods for detecting and measuring this NP. The techniques have increasing amounts of theoretical hadronic input. If NP is eventually detected in $B \rightarrow \pi\pi$ -- there is no evidence for it at present -- one will be able to distinguish $I=2$ and $I=0$, and measure its parameters, using these methods.

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(2005) 114007.

CAN ONE DETECT NEW PHYSICS IN $I=0$ AND/OR $I=2$ CONTRIBUTIONS TO THE DECAYS $B \rightarrow \pi\pi$?

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We study the effects of new-physics contributions to $B \rightarrow \pi\pi$ decays, which can be parametrized as four new complex quantities. A simple analysis is provided by utilizing the reparametrization invariance of the decay amplitudes. We find that six quantities can be reabsorbed into the definitions of Standard Model-like parameters. As a result, the usual isospin analysis provides only two constraints on new physics which are independent of estimates for the Standard Model contributions. In particular, we show that one is not sensitive to new physics affecting the $I=0$ amplitudes. On the other hand, $I=2$ new physics can be detected, and its parameters can be measured by using independent determinations of the weak phases. We obtain constraints on these new-physics parameters through a fit to the current experimental data.

Publicado em:

Physical Review D,
72 (2005) 036004.

REPARAMETRIZATION INVARIANCE OF B DECAY AMPLITUDES AND IMPLICATIONS FOR NEW PHYSICS SEARCHES IN B DECAYS.

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Publicado em:
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(2005) 094008.

When studying B decays within the Standard Model, it is customary to use the unitarity of the CKM matrix in order to write the decay amplitudes in terms of only two of the three weak phases which appear in the various diagrams. Occasionally, it is mentioned that those two weak phases can be used in order to describe any decay amplitude, even beyond the Standard Model. Here we point out that, when describing a generic decay amplitude, the two weak phases can be chosen completely at will, and we study the behavior of the decay amplitudes under changes in the two weak phases chosen as a basis. Of course, physical observables cannot depend on such reparametrizations. This has an impact in discussions of the SM and in attempts to parametrize new physics effects in the decay amplitudes. We illustrate these issues by looking at $B \rightarrow \psi K_S$ and the isospin analysis in $B \rightarrow \pi \pi$.

A STUDY OF LCP/TP BLENDS UNDER STATIONARY AND NON-STATIONARY SHEAR CONDITIONS: INFLUENCE OF THE LCP CONTENT AND PROCESSING TEMPERATURE

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Blends containing liquid crystalline polymers and thermoplastics have been a topic of great interest for the scientific community due to their excellent performance and properties and thus, promising use in industrial applications. For that reason, from the eighties until today, these systems were widely studied and characterized in terms of their mechanical, morphological, and rheological properties under stationary conditions but not under non-stationary ones which are, in fact, those most relevant to processing sequences. Thus, despite all the published work on this subject, there is still a need to study the response of the materials under the latter conditions.

The transient shear measurements performed on the blends of Rodrun LC3000 and PP showed an overshoot for the transient stress, the magnitude of which increases with increasing LCP content. This overshoot is attributed to the orientation and deformation of the LCP structures.

The results obtained for the blends by Large Amplitude Oscillatory Shear, LAOS, revealed to be highly sensitive (comparing with those observed in steady shear measurements) not only to the LCP content, but also to the processing temperature. From the rheological point of view an unusual behavior was observed for these systems, which was characterized by an increase of the viscosity and storage modulus with the increase of the LCP content at low frequencies, but a decrease at high frequencies. The traditional and well known decrease of steady shear viscosity and mechanical improvement, induced by the addition of liquid crystalline polymer to the thermoplastic, was also observed.

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Journal of Polymer Engineering, 25 (2005) 527.

INFLUENCE OF TYPE OF COMPATIBILIZER ON THE RHEOLOGICAL AND MECHANICAL BEHAVIOR OF LCP/TP BLENDS UNDER DIFFERENT STATIONARY AND NON-STATIONARY SHEAR CONDITIONS

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Polymer Science*, 98
(2005) 694.

The addition of small amounts of liquid crystalline polymers to thermoplastics leads to the formation of *in-situ* reinforced materials, with improved processability and mechanical properties. Nevertheless, the lack of adhesion between the thermoplastic and the liquid crystalline polymer often occurs, thus requiring the use of compatibilizers. In this case, the results of several previous works show that there is an improvement of strength, usually accompanied by a decrease of toughness and, thus, the interest of LCP/TP blends for industrial applications will certainly increase if both strength and toughness are obtained. Additionally, the emphasis of previous studies has been on the evaluation of the properties of the blend under stationary conditions and not under non-stationary ones which are, in fact, those most relevant to processing sequences. Thus, the present work focuses on the influence of type of compatibilizer on the mechanical and rheological properties of polypropylene/LCP blends, under non-stationary conditions. In terms of mechanical properties, the traditional increase of tensile strength was obtained for all compatibilizers, which was essentially due to the formation, during processing, of thinner and longer fibrils of LCP dispersed in the matrix than those observed for the non-compatibilized blends. Additionally, an improvement of the impact strength and flexural modulus was also observed for the blend in which a compatibilizer with an elastomeric nature was used. Rheologically, the experiments most sensitive to the structure were those performed in transient shear, with an increase of the transient stress (in the form of an overshoot) of different magnitudes being observed for the different compatibilizers.

CONVECTIVE PATTERNS UNDER THE INDO-ATLANTIC BOX

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Using fluid mechanics, we reinterpret the mantle images obtained from global and regional tomography together with geochemical, geological and paleomagnetic observations, and attempt to unravel the pattern of convection in the Indo-Atlantic “box” and its temporal evolution over the last 260 Myr. The “box” presently contains a) a broad slow seismic anomaly at the CMB which has a shape similar to Pangea 250 Myr ago, and which divides into several branches higher in the lower mantle, b) a superswell centered on the western edge of South Africa, c) at least 6 primary hotspots with long tracks related to traps, and d) numerous smaller hotspots. In the last 260 Myr, this mantle box has undergone 10 trap events, 7 of them related to continental breakup. Several of these past events are spatially correlated with present-day seismic anomalies and/or upwellings. Laboratory experiments show that superswells, long-lived hotspot tracks and traps may represent three evolutionary stages of the same phenomenon, i.e. episodic destabilization of a hot, chemically heterogeneous thermal boundary layer, close to the bottom of the mantle. When scaled to the Earth’s mantle, its recurrence time is on the order of 100–200 Myr. At any given time, the Indo-Atlantic box should contain 3 to 9 of these instabilities at different stages of their development, in agreement with observations. The return flow of the downwelling slabs, although confined to two main T boxes (Indo-Atlantic and Pacific) by subduction zone geometry, may therefore not be passive, but rather take the form of active thermochemical instabilities.

Publicado em:

*Earth and Planetary
Science Letters* 239
(2005) 233.

COLLOIDAL INTERACTIONS IN TWO-DIMENSIONAL NEMATIC EMULSIONS

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We review theoretical and experimental work on colloidal interactions in two-dimensional (2D) nematic emulsions. We pay particular attention to the effects of (i) the nematic elastic constants, (ii) the size of the colloids, and (iii) the boundary conditions at the particles and the container. We consider the interactions between colloids and fluid (deformable) interfaces and the shape of fluid colloids in smectic-C films.

Publicado em:

*Pramana - Journal of
Physics, 64 (2005)
991.*

REOLOGIA DE SUSPENSÕES LATEX/ CRISTAL LÍQUIDO LIOTRÓPICO

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O sistema liotrópico obtido a partir da dispersão de latex no cristal líquido (laurato de potássio (KL) + cloreto de decilamónio (DaCl) + água (H₂O)) apresenta um diagrama de fases complexo, onde foram identificadas duas fases nemáticas uniaxiais (uma nemática calamítica, N_C e uma nemática discótica, N_D) e uma fase nemática biaxial (N_{BX}) e, naturalmente (acima de uma dada temperatura que depende da concentração de látex), uma fase isotrópica (ISO).

Neste trabalho, apresenta-se o estudo do comportamento reológico do sistema latex/CL, para concentrações de latex de 0, 0,25, 0,5 e 1% (em peso da solução), e para uma gama de temperaturas dos 20 aos 51 °C. Para além da obtenção das curvas de fluxo da viscosidade em função da taxa de deformação de corte, $\eta(\dot{\gamma})$, em função da concentração de latex da solução e da temperatura do ensaio, apresenta-se uma estimativa da energia de activação, E_a, correspondente a cada fase presente na solução, numa determinada gama de temperaturas. Estas estimativas tiveram como objectivo verificar da possibilidade de obtenção de um diagrama de fases, baseada em medidas reológicas. Para as soluções de CL (0 % latex) e de 1% latex/CL verificou-se, regra geral, uma diminuição da E_a, quando se passa da fase N_C para a N_{BX} e desta para a N_D. No caso da solução 1% latex/CL a E_a volta a aumentar quando se passa da fase N_D para a fase isotrópica (ISO).

Publicado em:

e-rheo.pt, 5 (2005) 1.

FIELD ROTATIONS WIRE WITH POLYGONS OF EQUAL PERIMETER: MAGNETIC FIELD VERSUS MAGNETIC FLUX

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Instituto Superior de Engenharia de Lisboa

Publicado em:
*European Journal of
Physics*, 26 (2005)
783 – 790.

We compare the magnetic field at the center of and the self-magnetic flux through a current-carrying circular loop, with those obtained for current-carrying polygons with the same perimeter. As the magnetic field diverges at the position of the wires, we compare the self-fluxes utilizing several regularization procedures. The calculation is best performed utilizing the vector potential, thus highlighting its usefulness in practical applications. Our analysis answers some of the intuition challenges students face when they encounter a related simple textbook example. These results can be applied directly to the determination of mutual inductances in a variety of situations.

BRINCANDO COM O ASTROBLASTER.

Patrício, P.; Silva, J.P.

Instituto Superior de Engenharia de Lisboa

O “Astroblaster” é um brinquedo constituído por três bolas colocadas num eixo, no qual pode deslizar uma quarta bola. Deixando o conjunto cair para o chão, a quarta bola é projectada a uma velocidade incrível. Neste artigo discutimos a Física deste brinquedo e mostramos como ela nos levou desde as contas elementares até às fronteiras da investigação.

Publicado em:

Gazeta de Física, Vol. 28, Fasc. 2, (2005) 4.

ENTREVISTA A ANTHONY LEGGETT.

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Publicado em:

Gazeta de Física, Vol. 28, Fasc. 3, (2005) 18.

Anthony J. Leggett ocupa actualmente a “John D. and Catherine T. MacArthur Chair” e é Professor de Física no Center for Advanced Study da Universidade de Illinois (EUA). É membro do Departamento de Física desta Universidade desde 1983. É mundialmente conhecido como um especialista de física teórica das baixas temperaturas e o seu trabalho pioneiro sobre a superfluidade foi reconhecido com o Prémio Nobel da Física de 2003.

Anthony Leggett nasceu em Camberwell, Sul de Londres, em 1938. Terminou o bacharelato em Letras e Humanidades, na Universidade de Oxford, em 1959. Dois anos depois, obteve o bacharelato em Física, e em 1964 o doutoramento em Física Teórica, também em Oxford. Para além do Prémio Nobel da Física, foi galardoado com o Prémio Wolf, o Prémio John Bardeen, e o Prémio Paul Dirac, entre outros. O Professor Leggett é membro ou Fellow das mais prestigiadas sociedades científicas de todo o mundo.

Tivemos oportunidade de o entrevistar, por ocasião de uma visita a Lisboa em Junho de 2005, a convite do Centro de Física Teórica e Computacional da Universidade de Lisboa. Antes da nossa conversa, Anthony Leggett tinha apresentado duas palestras de âmbitos muito diferentes, intituladas “Testing the limits of quantum mechanics: motivation, state of play, prospects” e “Introduction to high energy low temperature physics”.

CARACTERIZAÇÃO DA ANISOTROPIA NO MANTO SÚPERIOR NA REGIÃO DOS AÇORES A PARTIR DO SPLITTING DAS ONDAS SKS

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The Azores archipelago occupies a lateral branch of the Mid-Atlantic ridge near the triple junction of 3 large tectonic plates, the North American, the Eurasian and the African 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. A better characterization of mantle anisotropy beneath is important to provide new insight in mantle anisotropy below this oceanic region. The several broadband stations of the Memorandum of understanding COSEA, located in Azores archipelago, offers an opportunity to study seismic anisotropy. Path-integrated anisotropy can be estimated most readily from shear waves that enter an anisotropic region with a know polarization as it is the case of the SKS and SKKS. To test a prediction of the anisotropy of the upper mantle beneath the Azores archipelago, we measure splitting of the waveforms of SKS and SKKS. Splitting observations have often, but not universally, indicated a fast axis parallel to the plate motions (Vinnik et al., 1992). Our preliminary SKS measurements beneath CMLA seem to contradict this result, and the average anisotropy must be small if it exists at all.

Publicado em:

Proceedings do 4^a Simpósio de Meteorologia e Geofísica da APMG., Associação Portuguesa de Meteorologia e Geofísica, 2005, p. 29.

LASER PROCESSING OF MAGNETIC OXIDES FOR APPLICATIONS IN SPINTRONICS

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Publicado em:
*Livro de resumos do
 “European Materials
 Research Society
 Spring Meeting, E-MRS
 2005 Spring Meeting”,
 Strasbourg, France,
 2005 (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/semiconductor interfaces, the development of these interfaces being one of the main technological challenges to be overcome before realistic devices can be fabricated. Therefore, much effort has gone into developing efficient and controlled methods for preparing ferromagnetic thin 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 in spintronic device applications.

Chromium dioxide (CrO_2) and magnetite (Fe_3O_4) are attractive compounds to use in these heterostructures since they have half-metallic band structures fully spin-polarised at the Fermi level. Furthermore, CrO_2 is strongly ferromagnetic at room temperature ($T_C \sim 393$ K) and magnetite is the half-metallic oxide with the highest known Curie temperature ($T_C \sim 850$ K), far above room temperature. Nevertheless, the synthesis of these thin films at low temperatures has been a difficult task either due to the metastable nature of CrO_2 or to difficulties in growing single phase thin films of stoichiometric magnetite.

In this paper, the fabrication of these thin films by laser-aided deposition methods (PLD and LCVD) and their properties are reviewed.

Partial funding by FENIKS contract (G5RD-CT-2001-00535) is acknowledged.

CVD OF CrO₂ THIN FILMS: INFLUENCE OF THE DEPOSITION PARAMETERS ON THEIR STRUCTURAL AND MAGNETIC PROPERTIES

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Magnetic materials exhibiting a high degree of spin polarization are being actively investigated for their potential use in spintronic devices. Among them, chromium dioxide (CrO₂) is very attractive because it is a half-metal fully spin polarized at the Fermi level with a high Curie temperature. However, CrO₂ is difficult to synthesise due to its metastability.

This work reports on the synthesis of CrO₂ thin films by chemical vapour deposition using chromium trioxide (CrO₃) and oxygen. Highly textured (200) CrO₂ films containing a small amount of Cr₂O₃ were grown on Al₂O₃ (0001) substrates. Films display a sharp magnetic transition at $T \sim 396$ K and a saturation magnetization of 1.95 $\mu\text{B}/\text{f.u.}$, close to the bulk value of 2 $\mu\text{B}/\text{f.u.}$ for the CrO₂. The influence of the deposition parameters on the structural and magnetic properties of the films is discussed.

Acknowledgement: This work is supported by the FCT (Portugal) contract POCTI/CTM/41413/2001.

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Livro de resumos do "3rd International Materials Symposium - Materiais 2005", Aveiro, Portugal, 2005 (comunicação em poster).

CAPTURING COLLOIDS IN 2D NEMATIC LIQUID CRYSTALS

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Publicado em:
*Livro de resumos da
"6th Liquid Matter
Conference", Utrecht,
Holanda, p. 106, 2005
(comunicação em
poster).*

We have studied numerically the behaviour of colloidal disk-like particles dispersed in two-dimensional nematic liquid crystals near structured or sculpted walls. Homeotropic boundary conditions were imposed at the wall and at the surface of the disk. It was found that the repulsion observed near a planar wall may shift into strong attraction in the presence of a cavity closely matching the shape and size of the colloid. By minimizing the Landau-de Gennes free energy, we were able to analyze in detail this *key-lock* mechanism for colloidal disks and spherocylindrical cavities of various length to depth ratios. We found that the attractions occur only for walls with cavities within a small range of the colloidal size and a narrow range of orientations with respect to the cavity's symmetry axis.

COLLOIDAL INTERACTIONS IN NEMATIC LIQUID CRYSTALS. THE INTERACTION OF COLLOIDS WITH A NEMATIC ISOTROPIC INTERFACE.

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Colloidal dispersions in nematic liquid crystals form a special class of colloids. The difference from ordinary colloids arises from the long-range orientational order of the liquid crystal molecules, described by the nematic director. In addition, topological defects of the director field may induce complex long-range forces between colloidal particles and, as a result, supermolecular structures are phenomena specific of colloidal nematics. Colloidal nematics are usually prepared in the isotropic phase. After cooling to a temperature below the NI transition, the colloids often segregate forming non uniform clusters. In general, topological defects stabilize the dispersion although in some cases they may help flocculation by producing attractive interactions. Here we review work on colloidal interactions in 2D nematic liquid crystals under a variety of conditions: homeotropic and planar anchoring as well as the interaction of colloids with various NI interfaces.

Publicado em:

Livro de resumos da "6th Liquid Matter Conference", Utrecht, Holanda, p. 113, 2005 (comunicação em poster).

OPTIMISATION OF THE PROCESSING CONDITIONS FOR COMPATIBILIZED RODRUN LC₃₀₀₀/PP BLENDS

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In previous presentations we have reported about the study performed in order to choose good compatibilizers and to find the optimum LCP and compatibilizer contents for Rodrun LC 3000/PP blends.

In this work we will present the optimization of the processing conditions, for this same system, performed with blends with two different compatibilizers and with the optimized LCP and compatibilizer contents. This optimization was performed by studying the influence of the different processing conditions, screw speed, output and temperature, on the final morphological, rheological and mechanical properties.

The evolution of the microstructure along the extruder length will be additionally presented, since it revealed to be quite sensitive to the application of the different processing conditions.

We concluded that lower screw speeds, as well as lower temperatures and intermediate outputs lead to higher mechanical performance of these blends.

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"2nd Annual European
Rheology Conference –
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Abril, Grenoble,
França, 2005
(comunicação oral).*

LANGUAGE EVOLUTION IN STRUCTURED POPULATIONS

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Simple models of language evolution are characterized by a pay-off that accounts for selection in communicative function, and by an error in learning, that measures the accuracy in language acquisition. In the mean field approximation, these models exhibit a “coherence threshold”, i.e., a minimal accuracy in the learning process is needed in order to evolve to a dominant language. In this work, we study the influence of the topology of contacts on the coherence threshold, by performing numerical simulations on structured populations (regular lattices, small world and scale free networks).

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Conference of the
European Physical
Society”, Berna, Suíça,
Julho de 2005
(comunicação em
poster).*

CONVECTIVE PATTERNS UNDER THE INDO-ATLANTIC BOX

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Suppl., Abstract S41C-
1021, 2005
(comunicação em
poster).

In this work, we reinterpret the images of the Indo-Atlantic mantle obtained from tomography studies together with geochemical, geological and paleomagnetic observations to unravel the pattern of convection in the Indo-Atlantic box and its temporal evolution over the last 260 Myr. Seismic tomography sections at different depths show that the Earth's mantle seems to be divided in two boxes by the subducted plates, the Pacific and the Indo-Atlantic boxes. The latter presently contains a) a broad slow seismic anomaly at the CMB which has a similar shape to Pangea 250 Myr ago, and which divides into several branches higher in the lower mantle, b) one superswell centered on the western edge of South Africa, c) at least 6 primary hotspots with long tracks related to traps, and d) numerous smaller hotspots. Moreover, in the last 260 Myr, this mantle box has undergone 10 traps events, 7 of them related to continental break up. Several of these past events are spatially correlated with present-day seismic anomalies and/or upwellings, suggesting episodicity. Laboratory experiments show that superswells, long-lived hotspot tracks and traps may represent three evolutionary stages of the same phenomenon, i.e. the episodic destabilization of a hot, chemically heterogeneous thermal boundary layer, close to the bottom of the mantle. When scaled to the Earth's mantle, the recurrence time of this phenomenon is on the order of 100-200 Myr. Also, at any given time, the Indo-Atlantic box should contain 3 to 9 of these instabilities at different stages of their development. This is in agreement with observations. The return flow of the downwelling slabs, although confined to two main boxes by subduction zone geometry, may therefore not be passive, but rather take the form of active thermochemical instabilities.

ELECTRICAL TRANSPORT PROPERTIES OF CHIRAL MOLECULAR CONDUCTORS; THERMOPOWER AND MAGNETOCHIRAL ANISOTROPY EFFECTS IN TETRATHIAFULVALENE-OXAZOLINE BASED CONDUCTORS.

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The preparation of chiral molecular conductors is currently a topic of high interest among the molecular materials research community. This interest is in a large way due to the fact that transport properties of chiral systems are predicted to display the electrical magnetochiral anisotropy as recently observed in single-walled carbon nanotubes. However the number of known chiral molecular conductors is still very restricted and the magnetochiral anisotropy is small a small effect difficult to measure.

Recently Avarvari et al. reported the first chiral molecular molecular conductors with metallic properties, based on Tetrathiafulvalene-Oxazoline derivatives, for which either the racemic, or the R and S enantiomers could be obtained.

In order to better characterize these chiral conductors we performed electrical magnetochiral anisotropy and thermoelectric power measurements which are described in this presentation. The magnetochiral measurements, made using a technique developed by us and able to easily detect effects down to 10^{-4} , revealed that the anisotropy in these materials is below this limit of detection.

Thermopower measurements for the racemic, R and S enantiomers of different families of chiral molecular conductors based on Tetrathiafulvalene-Oxazoline confirm the metallic behaviour of many of these materials in an extended temperature range in spite of shallow minima of resistivity as function of temperature often present.

Publicado em:

Livro de resumos do "Workshop on Molecular Materials 2005 - Research frontiers in molecular materials science", ITN, Sacavém, Portugal, 2005 (comunicação oral).

ELECTROCHEMICAL BEHAVIOUR OF TRIS(PYRAZOLYL)METHANE AND TRIS(PYRAZOLYL)METHANESUFONATE VANADIUM COMPLEXES

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In spite of their relevance in synthetic inorganic, bioinorganic and organometallic chemistries, vanadium complexes containing the N₃ tripodal ligands hydrotris(1-pyrazolyl)methane, and substituted ones, have not yet been the object of an electrochemical investigation.

We now report the results of our study of the electrochemical behaviour of new vanadium complexes, obtained by reaction of VO(OEt)₃ and VCl₃ towards HCp_z₃, HC(3,5-Me₂pz)₃, Li[SO₃Cp_z₃] and Li[SO₃C(3,5-Me₂pz)₃], carried out in 0.2M [Bu₄N][BF₄]/CH₂Cl₂, by cyclic voltammetry (CV) at a Pt-disc electrode and by controlled potential electrolysis (CPE) at a Pt-gauze electrode.

Such behaviours are discussed in terms of electron richness of the V centres and the electronic properties of the ligands.

This work has been partially supported by the IPL/41/2003 project, the POCTI (FEDER funded) programme and the Fundação para a Ciência e Tecnologia (FCT), Portugal.

Publicado em:

Livro de resumos do "VII Iberic Meeting of Electrochemical and XIII Meeting of the Portuguese Electrochemical", Covilhã, Portugal, 2005 (comunicação em poster).

NEW TRIS(PYRAZOLYL)METHANE RHENIUM AND VANADIUM COMPLEXES: SYNTHESIS AND CATALYTIC APPLICATION IN ALKANE OXIDATION

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The chemistry of tris(pyrazolyl)methane transition metal complexes is attracting a high interest in particular due to the discovery of their application in catalysis and synthetic organometallic chemistry. Nevertheless, the coordination chemistry of tris(pyrazolyl)methanes at rhenium and vanadium sites still remains an underdeveloped field.

Herein we report the synthesis of new rhenium and vanadium complexes with the N₃ tripodal neutral ligand hydrotris (1-pyrazolyl) methane (HCpz₃; pz = pyrazolyl) or its derived disubstituted hydrotris (3,5-dimethyl-1-pyrazolyl) methane [HC(3,5-Me₂pz)₃], e.g., [ReCl₃{HC(3,5-R₂pz)₃}] (R = H or Me) or [VO(HCpz₃)](BF₄)₃, respectively. In some cases we have observed the conversion of the tris (pyrazolyl) methane into the corresponding pyrazole, as e.g., in [ReCl₃(NCMe)(Hpz)₂]. The complexes have been characterized by IR and multinuclear NMR spectroscopies, FAB-MS spectrometry and elemental analysis. We also report the study of the catalytic behaviour of these rhenium and vanadium complexes in the peroxidative oxidation of alkanes to the corresponding alcohols and ketones. Turnover numbers and yields are indicated.

This work has been partially supported by the IPL/41/2003 project, the POCTI (FEDER funded) and the PRODEP programmes and by the Fundação para a Ciência e Tecnologia (FCT), Portugal.

Publicado em:

Livro de resumos da "5th International School of Organometallic Chemistry", Camerino, Itália, 2005 (comunicação em poster).

NEW TRIS(PYRAZOLYL)METHANE VANADIUM COMPLEXES: SYNTHESIS AND CATALYTIC ACTIVITY

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Publicado em:
Livro de resumos da conferência "2nd Aquachem – Green Chemistry a Solution for the World", Almeria, Espanha, 2005 (comunicação em poster).

Although some vanadium compounds can display interesting catalytic properties, their application in catalysis is still an underdeveloped field of research. The conversion of alkanes into oxygenated derivatives (namely of cyclohexane into cyclohexanol and cyclohexanone) has been extensively studied in view of the high industrial significance of such products.

Moreover, the chemistry of tris(pyrazolyl)methane transition metal complexes is currently attracting a high interest in particular due to the discovery of their application in catalysis and synthetic organometallic chemistry. Nevertheless, the coordination chemistry of tris(pyrazolyl)methanes at vanadium sites still remains very little explored.

Herein we report the synthesis of new vanadium(IV) complexes with the N₃ tripodal anionic tris(1-pyrazolyl)methanesulfonate SO₃Cpz₃⁻ (pz = pyrazolyl) ligand, which are water-soluble and can act as catalysts in the peroxidative oxidation of cyclohexane to cyclohexanone and cyclohexanol, by H₂O₂, under mild conditions in aqueous medium.

The new complexes have been characterized by IR and multinuclear NMR or EPR spectroscopies, FAB-MS spectrometry and elemental analysis. For the catalytic studies the turnover numbers and yields are indicated.

This work has been partially supported by the AQUACHEM Project RTN n^o MRTN-CT-2003-503864, the IPL/41/2003 project, the POCTI (FEDER funded) program and by the Fundação para a Ciência e Tecnologia (FCT), Portugal.

ACOUSTIC AND PSYCHO-ACOUSTIC STUDY OF THE NOISE INDUCED BY THE DIFFERENT 25TH APRIL BRIDGE TRANSPORTATION MEANS

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The 25th April Bridge is a complex structure regarding noise emission since it contains two separate sound sources: road traffic and railway traffic. The analysis of the noise generation mechanisms has to consider the mixed structure made of a concrete viaduct and of a suspended metal structure. The aim of the work described in this paper was to fully determine the influence of the noise induced by the different bridge transportation means on the acoustical environment in the surrounding areas and on the perception of the overall and of the different contributing transportation noises by the local population. The correlation between these two facts led to the development of a “Nuisance Model” which was considered adequate to the present situation. Results of the acoustical survey and of the psycho-acoustical analysis carried out on representative samples of the local population are shown and discussed. It was found out that although the railway traffic is usually referred as the one with the less social impact in the bridge vicinity area, the psycho-social impact is more important than that corresponding to the road traffic, especially at night.

Publicado em:

“AAM - Environmental Acoustics”,
Proceedings of the Iberian Meeting on Acoustics and XXXVI Spanish Congress on Acoustics - TECNIAÚSTICA 2005, Terrassa, Spain.

PRELIMINARY RESULTS FOR THE MAGMATIC FLOW PATTERN OF THE FOZ DA FONTE SILL BY AMS

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Publicado em:
Livro de resumos da conferência "APMG 2005 - 4.º Simpósio de Meteorologia e Geofísica da APMG", Sesimbra, Portugal, 2005 (comunicação oral).

This study focuses on the significance of the anisotropy of magnetic susceptibility (AMS) in the Foz da Fonte sill, north of Cabo Espichel. The Foz da Fonte sill is a dolerite emplaced within the uppermost Lower Cretaceous sediments of the southern part of the Lusitanian Basin (Arrábida sector), with an average thickness of 8m. The outcrop is presently exposed on the coast, slightly dipping to NW, with a rectangular shape of 35 m x 70 m, approximately.

The AMS data was used to constrain the types of magma feeding by identification of magmatic flow pattern. Two principal modes of feeding systems for sheet intrusions and assuming a single magmatic pulse are: (1) pipe feeder in which magma supply originates from a single vertical pipe or, (2) dyke feeder in which magma supply originates from a vertical dyke. In the pipe feeder model it is expected a magmatic radial flow away from the feeder, while in the dyke feeder model it is expected a magmatic parallel flow away from the dyke.

The samples for the present study were collected from 11 stations throughout the central part of the sill ceiling. At least 5 specimens for station were obtained, giving a total of 65 specimens. The average magnetic susceptibility is $k = 78 \pm 16$ (10^{-3} SI) and the shape of ellipsoid of susceptibility is prolate with magnetic lineation $L = 1.022 \pm 0.002$ and magnetic foliation $F = 1.014 \pm 0.008$. The average degree of magnetic anisotropy is low, $P = 1.036 \pm 0.015$. Magnetic fabric is triaxial.

The lack of increase of P with k suggests that interaction anisotropy is not the dominating component of magnetic anisotropies in these rocks.

Optical analysis of 26 oriented images from 5 stations (7 thin sections) shows a strong correlation between magnetic lineation and preferred orientation (distribution) of Fe, Ti oxides. Magnetic lineation is interpreted as parallel to the magma flow plane.

Thermomagnetic analysis under argon atmosphere (susceptibility versus temperature) shows one principal magnetic phase with Curie temperature of 570 ± 14 and some vestiges of a minor phase with Curie temperature below 4000°C .

The measured magnetic properties (bulk and anisotropy susceptibilities) are very consistent and steady across the sill.

In all stations magnetic lineation has a general WNW - ESE orientation. It is extremely well defined with $K_1 = 120^\circ/1^\circ$ (direction/inclination) and very small ellipse of confidence with semi-axes $e_{13} = 2^\circ$ and $e_{21} = 4^\circ$.

The magnetic foliation plane is also very well defined and with the exception of one station, it is everywhere sub-horizontal and slightly imbricated relative to the sill ceiling, Minimum AMS axis, $K_3 = 206^\circ/85^\circ$ and semi-axes of confidence are $e_{13} = 2^\circ$ and $e_{23} = 5^\circ$.

Systematic lateral variations of magnetic lineation or magnetic foliation planes are not observed.

Conclusions

The steadiness of the WNW - ESE trending magnetic lineation in every different station, points to a uniform flow direction compatible with: (1) a planar source, like a dyke feeder, with an average NNE - SSW orientation or, (2) a distant igneous source. The observed orientation of the systematic imbrication angle between the top of the sill and the magnetic foliation plane suggests the possibility of an injection from a source located WNW, offshore. Nevertheless this is an hypothesis that needs to be carefully tested by further sampling in different parts and levels of the sill.

TOMOGRAFIA SÍSMICA CRUSTAL DA CRISE SÍSMICA DO FAIAL DE JULHO DE 1998

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*Livro de resumos da
conferência "APMG
2005 - 4.º Simpósio
de Meteorologia e
Geofísica da APMG",
Sesimbra, Portugal,
2005 (comunicação
oral).*

O sismo de 9 de Julho de 1998 desencadeou uma crise sísmica, responsável pela geração de milhares de sismos nas semanas seguintes. Na sequência de outros estudos entretanto efectuados, levou-se a cabo um estudo de tomografia sísmica local, aplicado à crise sísmica do Faial. Foram seleccionados 735 eventos, registados nas estações localizadas nas ilhas do Faial, Pico e São Jorge, correspondentes a eventos com localização estável e bem constrangida.

A estrutura 3D de velocidades V_p final, indica a presença de uma forte anomalia positiva nas velocidades na zona de principal concentração de eventos, enquanto que na zona do canal entre o alinhamento Pico-Faial e São Jorge surge em uma anomalia negativa profunda mais difusa. Um corte em profundidade revela que a sismicidade tende a ficar confinada no contacto entre estas duas anomalias, podendo sugerir a presença de um sistema de falhas como causa destes eventos. O modelo V_p/V_s tende a confirmar esta ideia, pois o valor desta razão é razoavelmente uniforme excepto nas zonas de localização de hipocentros, onde surgem fortes anomalias positivas e negativas. Numa zona de falhas é de esperar uma anomalia na razão V_p/V_s , em virtude de serem zonas mais frágeis, por vezes com intrusão de fluidos, conduzindo a variações significativas na razão de Poisson.

Estes resultados estão ainda a ser interpretados, nomeadamente no que respeita à forma das anomalias nas velocidades V_p , e na alternância das anomalias de V_p/V_s .

MEDIDAS MINIMIZADORAS DE RUÍDO

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As estratégias de controlo de ruído, sejam para implementação em espaço fechado ou em espaço aberto, determinam uma acção conjunta ao nível das fontes poluidoras, do meio de propagação das ondas sonoras e dos receptores potencialmente afectados. Assim, a eficácia da implementação de Medidas Minimizadoras de Ruído justifica a elaboração de planos globais que visem a redução dos níveis sonoros existentes e/ou previstos em determinado local. Em termos de ambiente exterior, são os Planos de Redução de Ruído que devem ser implementados, tendo por base os valores do índice de ruído ambiente existentes e/ou previstos, a caracterização das fontes sonoras e a sensibilidade dos usos e das ocupações do solo existentes. Em termos laborais, devem ser implementados Planos de Preservação da Audição, que terão em linha de conta não só os níveis sonoros existentes e/ou previstos, como também as características auditivas individuais de cada trabalhador. A Engenharia Acústica tem vindo a desenvolver diversas ferramentas e metodologias de medição e análise dos campos sonoros, de forma a permitir, com eficácia, estabelecer as melhores e as mais adequadas Medidas Minimizadoras de Ruído para cada situação concreta.

Publicado em:

"II Jornadas Técnicas de Segurança, Higiene e Saúde no Trabalho da ANA - Aeroportos de Portugal, SA", Ponta Delgada, Açores, 2005 (comunicação oral).



07

MATEMÁTICA

Anuário Científico 2005

ISEL

NOVO MODELO DE ENSINO DE MATEMÁTICA EM ENGENHARIA

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O ensino baseado apenas numa estrutura logicamente coerente que normalmente se inicia com a apresentação formal de axiomas, seguida por teoremas e terminando algumas aplicações matemáticas dos conceitos, permite uma boa planificação da estrutura do curso, normalmente baseada na apresentação expositiva dos assuntos, cobrindo todos os temas relevantes. No entanto esta metodologia tem a desvantagem de ser inflexível na adaptação aos modos de ser e de pensar de cada aluno.

Na maioria dos alunos, este sistema de ensino apenas produz uma aprendizagem centrada na memorização de umas quantas fórmulas, e procedimentos, a serem esquecidos após os exames. É neste contexto que se torna importante a busca de alternativas didáticas. Uma das fontes para procurar ideias sobre como melhorar a compreensão dos alunos é o entendimento de como é produzido o conhecimento matemático.

Publicado em:

*E-ciência Magazine,
n.º 23, Especial
Ensino da Matemática
em Portugal, Abril
2005*

INTERPRETAÇÃO ALGÉBRICA DO MÉTODO DOS MÍNIMOS QUADRADOS

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*CienTífica – Newsletter
da Texas Instruments,
Fall 2005.*

O método dos mínimos quadrados é uma técnica, muito difundida, para o cálculo de estimativas de parâmetros e de ajuste de dados. É um das técnicas mais antigas da estatística moderna e foi divulgada em 1805, pelo matemático francês Legendre (1752-1833). No entanto constatou-se que este método é mais antigo. Depois da publicação de Legendre, o famoso Matemático alemão, Gauss (1777-1855), publicou em 1809 um trabalho (*Theoria motus corporum coelestium in sectionibus conicis Solem ambientium*), onde reclamava para si a descoberta prévia deste método, tendo-o desenvolvido em 1795. Actualmente, o método dos mínimos quadrados é usado para determinar ou calcular os valores numéricos dos parâmetros para ajustar uma função a uma colecção de dados e caracterizar as propriedades estatísticas de estimativas. Esta técnica sofreu evoluções, dando origem a técnicas mais complexas, tais como os Métodos de Projecção, ou o Método dos Mínimos Quadrados Ponderados, constituindo um processo de cálculo para corrigir metodicamente resultados experimentais ou de medições, com vista à obtenção do seu valor mais provável.

O ENSINO DA MATEMÁTICA ASSISTIDO POR COMPUTADOR NUM CURSO DE ENGENHARIA

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Com esta comunicação apresentámos o projecto 2AMAC – Apoio na Aprendizagem de Matemática Assistido por Computador – no contexto do ensino da Matemática no curso de Engenharia Civil no ISEL. Mostrámos, também, de que forma este projecto contribui para uma melhoria da qualidade de ensino nas disciplinas de Análise Matemática I e Análise Matemática II do curso de Engenharia Civil, recorrendo à utilização de tecnologias de e-Learning/b-Learning, considerando as especificidades próprias para o Ensino Superior, utilizando uma abordagem diferenciada das abordagens comuns ao problema do e-Learning.

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*VI PMATE-
Universidade de
Aveiro.*

MAPPING STORES AND PRODUCTS FOR ASSORTMENT DECISIONS

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*Proceedings of the
 10th International
 Symposium on
 Logistics (2005), pp.
 446-451.*

Different stores exhibit different acquisition patterns for different assortments. Optimising the match stores-assortments has an evident impact in stores' performance, which retailers naturally seek.

In order to obtain a satisfactory solution to the assortment problem both the assortment composition and allocation (product-store) decisions have to be established. This may be particularly complex when diversity is present in product variety as well as in stores' heterogeneity. This work presents the results obtained in an exploratory analysis meant to support wine assortment decisions in a supermarket chain. In order to deal with stores' heterogeneity a clustering procedure is used, based on stores' characteristics, location attributes and consumers' profiles. In this case we use the estimation of a mixture model as a clustering tool.

The wines are also clustered considering two main dimensions: production region and price.

A preference measure is then proposed which links clusters of supermarkets and wine groups. This may also be viewed as a measure of attractiveness when considered from the wines' side.

Finally using a Multidimensional Scaling procedure (ALSCAL algorithm) a map is constructed that pictures the preference/attractiveness of stores and products. This map helps to delineate a preliminary assortment solution based on proximity measures which further analysis may help to improve.

COMPARAÇÃO DE DOIS MODELOS MDS-UNFOLDING: UMA APLICAÇÃO PRÁTICA

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Tipicamente o Multidimensional Scaling (MDS) Unfolding é usado na modelação de dados de preferências: os dados iniciais são valores de preferência de diferentes indivíduos sobre um conjunto de objectos e o objectivo é a representação de indivíduos e objectos num mesmo espaço euclídeo comum (usualmente bi-dimensional), onde, as distâncias indivíduos-objectos espelham as preferências.

Neste trabalho desenvolve-se uma aplicação de MDS Unfolding no âmbito de um problema de constituição e afectação de diferentes sortidos a diversas lojas de uma cadeia de supermercados. Os dados são relativos a uma classe de produtos – vinhos nacionais. Os modelos de MDS Unfolding aplicam-se com base numa medida de atractividade/preferência de grupos homogéneos de lojas, por tipos de vinho, medida essa que se obtém através de valores de vendas observados durante um ano. A configuração final, representando grupos de lojas vs tipos de vinho, insere-se na perspectiva de desenvolvimento de uma ferramenta de apoio à tomada de decisões de constituição de sortidos de vinho, diferenciados por lojas.

Várias propostas de modelação MDS-Unfolding podem ser consideradas. Neste trabalho utilizam-se o algoritmo ALSCAL (Takane, Y. and D. Leeuw, 1977. "Nonmetric individual differences multidimensional scaling: an alternating least squares method with optimal scaling features". *Psychometrika* 42: 7-67), concebido para problemas de MDS em geral e o PREFSCAL (Busing, F., Groenen, P. and Heiser, W., 2001. "Avoiding degeneracy in multidimensional unfolding by penalizing on the coefficient of variation." Manuscript accepted for publication.) desenvolvido especificamente para problemas de Unfolding. Através da aplicação que se apresenta ilustra-se a comparação dos dois processos e correspondentes resultados.

Publicado em:

*XIII Congresso da
Sociedade Portuguesa
de Estatística, Ericeira,
2005*

MULTI-OBJECTIVE OPTIMIZATION OF STRUCTURES TOPOLOGY BY GENETIC ALGORITHMS

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Publicado em:
*Elsevier, Advances in
Engineering Software,
36, (2005), 21-28*

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.

MULTI-OBJECTIVE TOPOLOGY OPTIMIZATION OF STRUCTURES USING GENETIC ALGORITHMS WITH CHROMOSOME REPAIRING

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Pina, Heitor¹

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2 DEETC-ISEL

In this work a genetic algorithm for multi-objective topology optimization of linear elastic structures is developed.

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 to be sorted by its domination properties and a filter is defined in order to retain the Pareto solutions.

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 chromosomes satisfying this propriety, to create corresponding crossover and mutation operators which preserve volume and to develop a repairing mechanism for chromosomes leading to non admissible structures.

Numerical applications involving two and three objective functions in 2D and two objective functions in 3D are employed as a test for the computational model developed.

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

Publicado em:

*6th World Congress of
Structural and
Multidisciplinary
Optimization, Rio de
Janeiro, 30 May - 03
June 2005, Brasil.*

PERSONALIZED FILTERING SYSTEMS BASED ON THE MULTI-METHODS COMBINATION

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We propose a modular platform to support the development of personalized filtering systems. According to our proposal, filtering systems can be constructed through the integration of different modules and changes on specific parameters. We also introduce a hybrid approach to improve filtering performance based on the combination of content and collaborative filtering, which suppresses the weaknesses of each traditional approach.

Publicado em:

*AC 2005, Proceedings
of the IADIS
International
Conference on Applied
Computing, Feb. 22-
25, 2005 - Algarve,
Portugal, 312-361*

MYTV: SISTEMA PERSONALIZADO DE TELEVISÃO

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Abordam-se os requisitos gerais de um sistema personalizado de televisão, no qual os utilizadores registados seriam alertados de programas interessantes, existentes no fluxo de programas, disponíveis num sistema de televisão por cabo.

Publicado em:
JETCo5, ISEL
Novembro de 2005

A MODULAR PLATFORM APPLICABLE TO ALL STATISTICAL RETRIEVAL MODELS

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This paper proposes a standard testing platform for Information Retrieval (IR) that can be used for testing different IR statistical models in a controlled environment or in the Web. The development of a standard system avoids the effort of developing a specific testing system to validate each method or model on the IR field of activity, working as a common platform. Examples of applications on filtering, classification and retrieval of information are presented.

Publicado em:

ITA05- Proceedings of the International Conference on Internet Technologies & Applications, de 7 a 9 de Setembro de 2005 em Wrexham, País de Gales
<www.newi.ac.uk/computing/research/ita05/>

MÉTODOS ESTATÍSTICOS PARA RECUPERAÇÃO DE INFORMAÇÃO

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É abordado o problema dos modelos de recuperação de informação, sob o ponto de vista estatístico, no sentido de estabelecer relações entre os diferentes algoritmos e apresentar uma visão unificada dos diferentes modelos com base em métodos estatísticos. É proposta uma notação comum para os mesmos conceitos apresentados por modelos diferentes evitando-se assim a grande diversidade das notações existentes, identificando-se os requisitos para um índice flexível capaz de fornecer matéria-prima para todos os modelos de pesquisa com base nas propriedades estatísticas dos documentos.

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JETCo5, ISEL

Novembro de 2005

FUSION METHODS TO FIND WEB COMMUNITIES

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We propose a new method that identifies communities based on the combination of different approaches (context and link analyses) using stable information user's needs (profiles) and documents (as author's profile). We discuss the application of standards and identify gaps and needs in the process of web's communities identification.

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*Proceedings of the
IADIS International
Conference on Web
Based Communities
05, Feb. 2005 -
Algarve, Portugal,
331-334*

COMBINAÇÃO DE MÉTODOS PARA PESQUISA DE INFORMAÇÃO

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Pretendem investigar-se diversos caminhos para combinar métodos de pesquisa por forma a melhorar o desempenho dos sistemas, oferecendo uma nova perspectiva da investigação dos sistemas de pesquisa, à descoberta da melhor estratégia, propondo um método baseado na combinação de três modelos: textual, ligações e de classificação.

Publicado em:
JETC05, ISEL
Novembro de 2005

WEB SERVICES FOR INFORMATION RETRIEVAL

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The idea developed in this paper is the creation of standard, information retrieval modules, in a distributed manner in order to create testing systems to validate methods and algorithms. An investigator in information retrieval area can construct a test retrieval system just by integrating different modules and manipulating the input of the variables of each module.

Publicado em:

*ITCC 05- Proceedings
of the International
Conference on
Information
Technology: Coding
and Computing,
Volume II, 497-502 –
Las Vegas – April
2005*

TERCEIRA GERAÇÃO DE SISTEMAS DE PESQUISA DE INFORMAÇÃO

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Pretende-se discutir e fundamentar um conjunto de ideias necessárias para o desenvolvimento de sistemas de pesquisa de informação com o objectivo de melhorar o desempenho dos mesmos. Assuntos como a personalização, perfil, interfaces de ajuda, uso de sistemas de classificação e contextualização da pesquisa são analisados e discutidos numa abordagem que permite integrar de uma forma unificada as suas potencialidades.

Publicado em:
JETCo5, ISEL
Novembro de 2005
(2005)

MAIN RETRIEVAL SYSTEMS' PARAMETERS ANALYZE

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Publicado em:
AC 2005, Proceedings of the IADIS International Conference on Applied Computing, Feb. 22-25, 2005 - Algarve, Portugal, 344-351

We explore retrieval effectiveness of vectorial, link analyses, probabilistic and classification retrieval system's parameters and compare the different performance in a controlled environment (using WT10g collection from TREC). Main retrieval parameters are captured: (1) retrieval methods (e.g., vectorial, link analyses, probabilistic and classification); (2) main internal system parameters (e.g., query length, URL length, phrase, feedback, index); (3) and also internal system parameters combination (e.g., combination of different query and URL lengths, phrase, feedback and index). We concluded about the most important parameters, retrieval method performance and the fact that the combination can improve the results. We have analyzed several cases from around 500 retrieval systems using our own modular platform, WebSearchTester.

LINGUAGEM PARA MODELAÇÃO DE SISTEMAS DE PESQUISA DE INFORMAÇÃO

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O presente trabalho pretende abordar o problema da falta de uniformização de conceitos, fórmulas e parâmetros na área da pesquisa de informação, introduzindo uma linguagem própria com base nos mecanismos de extensão do UML, a qual serve de base à construção de modelos abstractos para a PI. Estes modelos constituem um conjunto de bibliotecas cuja integração numa infra-estrutura permite construir sistemas de pesquisa de informação de uma forma simplificada, modular e uniforme.

Publicado em:

JETCo5, ISEL

Novembro de 2005

THE NEXT GENERATION OF INFORMATION RETRIEVAL APPLICATIONS

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We describe an Information Retrieval (IR) framework to cover the most relevant IR models based on statistics and link properties of the documents. We also propose to use the same framework for IR, filtering and classification process.

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*MCCSIS05 - IADIS
Multi Conference on
Computer Science and
Information Systems,
Maio de 2005.
<[http://www.iadis.org/
multi2005](http://www.iadis.org/multi2005)>*

OPTIMIZAÇÃO DE DELINEAMENTOS EM ESCADA SIMPLES

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Nestes delineamentos consideram-se u factores com encaixe sucessivo. A solução usual, de para cada nível do primeiro factor se considerar o mesmo número de níveis do segundo factor e assim sucessivamente, conduz a um número excessivo de tratamentos e a pouca informação sobre os primeiros factores. Como alternativa, pode-se considerar u sub-delineamentos em que no primeiro só há ramificação ao nível do primeiro factor, no segundo ao nível do segundo factor e assim sucessivamente. O número de tratamentos deixa de ser o produto do número de níveis para passar a ser a soma. Consegue-se assim distribuir melhor a informação recolhida pelos vários factores.

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Congresso Anual da
SPE (2005),
p. 247-253*

OPTIMIZATION OF NESTED STEP DESIGNS

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The number of treatments in a balanced nested design is the product of the number of levels in each factor. This number may be too large. As an alternative, in nested step designs there are as many sub-designs as factors plus one last sub-model used for error estimation. In each sub-design the branching is done only for the corresponding factor. The numbers of treatments is now the sum of the factor levels plus one. Moreover the amount of information for the different factors is more evenly distributed. We present a method to minimize the sum of the estimated variances of the estimators of the variance components.

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Biometrical Letters,
42 - 2 (2005),
p. 143-151

WIND SPEED PREDICTION USING ARTIFICIAL NEURAL NETWORKS

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In this paper the problem with the introduction of a large quantity of wind generators on the electric grid is presented. A method based in artificial neural networks (ANN) is used to predict the average hourly wind speed. The study starts by choosing the patterns set length to predict de wind speed. The ANN structure and the learning method are chosen as well as the dimensions of the sets of data, training, validation and test. The ANN is tested to archive an acceptable ANN based model. This model is afterwards used to predict the wind speed. The results archived are discussed and the future work perspectives are present.

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WSEAS Transactions on Systems, Vol. 4, N.º. 4, 2005, pp. 379-384.

RADIAL BASIS FUNCTION NETWORKS FOR WIND SPEED PREDICTION

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Conference on
Environment,
Ecosystems and
Development (EED'05),
Venice (Italy), 2-4
November, 2005*

The introduction of a large quantity of wind generators on the Portuguese electric grid, will produce the effect of having a large percentage of installed power whose production is not controllable. The consequence is a major difficulty to the grid operator in dealing with power availability and oscillations in the frequency. There is the urgent need of a reliable tool for estimating the expected value of the daily power produced by the wind generators in order to elaborate hourly and daily forwarding-dispatches. Artificial neural networks (ANN) are being used as a model able to predict the average hourly wind speed. However most of the work applying neural networks to wind speed prediction uses Multi-Layer Perceptrons (MLP) or the recurrent version of them. This work introduces Radial Basis Function networks (RBF) for wind speed prediction showing that this model of neural networks are more suitable for the task at hand, in terms of on-line decisions, and more efficient to train than MLP. The experiments are made with real-world data.

POSITIVE-DEFINITENESS, INTEGRAL EQUATIONS AND FOURIER TRANSFORMS

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We show that positive definite kernel functions $k(x,y)$, if continuous and integrable along the main diagonal, coincide with kernels of positive integral operators in $L^2(\mathbb{R})$. Such an operator is shown to be compact; under the further assumption that $k(x,y)$ converges to zero in infinity it is also trace class and the corresponding bilinear series converges absolutely and uniformly. If $k^{1/2}(x,y)$ is in $L^1(\mathbb{R})$, all these results are carried through to a 'rotated' Fourier transform of k which is the kernel of a compact positive operator and is represented by the absolutely and uniformly convergent series of Fourier transforms of eigenfunctions. The trace of the operator is an invariant under Fourier transforms.

Publicado em:

*Journal of Integral
Equations and
Applications, Volume
16, Number 1, Spring
2004*

PHASE DYNAMICS AND PARTICLE PRODUCTION IN REHEATING

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(2005) 083515

We study a simple model of a massive inflaton field ϕ coupled to another scalar field χ with interaction term $g \phi^2 \chi^2$. We use the theory developed by Kofman *et al.* (Phys. Rev. D **56** (1997) 3258 [arXiv:hep-ph/9704452]) for the first stage of preheating to give a full description of the dynamics of the χ field modes, including the behaviour of the phase, in terms of the iteration of a simple family of circle maps. The parameters of this family of maps are a function of time when expansion of the universe is taken into account. With this more detailed description, we obtain a systematic study of the efficiency of particle production as a function of the inflaton field and coupling parameters, and we find that for $g \leq 3 \cdot 10^{-4}$ the broad resonance ceases during the first stage of preheating.

(IN)STABILITY OF QUASI-STATIC PATHS OF SOME FINITE DIMENSIONAL SMOOTH OR ELASTIC-PLASTIC SYSTEMS

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In this paper we discuss some mathematical issues related to the stability of quasi-static paths of finite dimensional mechanical systems that have a smooth or an elastic-plastic behaviour. The concept of stability of quasi-static paths used here is essentially a continuity property relatively to the size of the initial perturbations (as in Lyapunov stability) and to the smallness of the rate of application of the external forces (which here plays the role of the small parameter in singular perturbation problems). A related concept of attractiveness is also proposed. Sufficient conditions for attractiveness or for instability of quasi-static paths of smooth systems are presented. The Ziegler column and other examples illustrate these situations. Mathematical formulations (plus existence and uniqueness results) for dynamic and quasi-static elastic-plastic problems with linear hardening are recalled. A stability result is proved for the quasi-static evolution of these systems.

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*Journal of Physics:
Conference Series 22,
International
Workshop on
Hysteresis and Multi-
scale Asymptotics
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RECIPROCAL AND RELATED THEOREMS FOR NEMATIC LIQUID CRYSTALS

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Reciprocal and related theorems are considered for uniaxial and biaxial nematic liquid crystals. In the general case, where the directors of real and reciprocal materials are assumed to coincide, integral relations between velocity and stress fields of the real and reciprocal materials are obtained. Simplified expressions are also obtained for the high viscosity and elasticity limits.

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*International Journal of
Engineering Science,*
43 (2005) 1185-1205

FLOW OF A NEMATIC LIQUID CRYSTAL NEAR THE LEADING EDGE OF AN INFINITE PRISM

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Flow of a nematic liquid crystal in an infinite wedge bounded by side-walls $\theta = \pm\alpha$ (with no-slip condition) is considered. The fluid is contained in the region $0 \leq r < +\infty$, $-\alpha \leq \theta \leq \alpha$ and $-\infty < z < +\infty$ ($0 \leq \alpha \leq \pi$). The near tip velocity field is assumed to have the form $v_i(r, \theta) = r^\lambda F_i(\theta)$ ($i = r, \theta, z$) as r tends to zero. We investigate the dependence of eigenvalues λ and functions $F_i(\theta)$ on the tilt angle, $G(\theta)$, between the director field and the plane $z = c$ ($c \in \mathbb{R}$) and on the included angle 2α of the wedge shaped prism. Two kinds of nematic liquid crystal are considered as examples: MBBA and PAA near 25 °C and 125 °C, respectively. In general, when $0 < G(\theta) < \pi/2$ the liquid crystalline material is curvilinear anisotropic and no symmetry properties are found. Here all velocity field components are coupled. This coupling reduces the magnitude of the leading order eigenvalue and the one with smallest real part is purely real for any wedge included angle. However, complex eigenvalues can occur for the next eigenvalues ordered in terms of the magnitude of the real part. Thus, if we impose the appropriate behaviour on the far field velocity, so it is orthogonal to the eigenvectors associated with the first real eigenvalues, the remaining flow fields may display eddies.

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The Quarterly Journal of Mechanics and Applied Mathematics (Oxford University Press), 58 (2005) 503-533

TOPOLOGICAL INVARIANTS IN FORCED PIECEWISE-LINEAR FITZHUGH-NAGUMO-LIKE SYSTEMS

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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 and we exhibit numerical results about maps with the same topological entropy, that suggest the existence of a relation between the parameters A and θ , when T is fixed.

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Chaos, Solitons & Fractals 23 (2005) 1553-1565

BIFURCATIONS ASSOCIATED WITH THE FITZHUGH-NAGUMO MAPS

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The FitzHugh-Nagumo-like systems are of fundamental importance to the understanding of the qualitative nature of nerve impulse propagation. Our work provides a numerical investigation of bifurcations associated with a family of piecewise differentiable canonical maps for a planar FitzHugh-Nagumo system. We describe the bifurcation structure of the maps with the variation of the parameters.

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Nonlinear Dynamics
(2005) 1-12

SYMBOLIC DYNAMICS IN THE STUDY OF BURSTING ELECTRICAL ACTIVITY

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Many cells exhibit a complex behavior, characterized by brief bursts of oscillatory activity interspersed with quiescent periods during which the membrane potential changes only slowly. This behavior is called bursting. The interpretation of bursting in terms of nonlinear dynamics is one of the recent success stories of mathematical physiology and provides an excellent example of how mathematics can be used to understand complex biological dynamical systems. In the present paper we study a map, that replicates the dynamics of bursting cells. Using symbolic dynamics we characterize the topological entropy of the chaotic bursts and we analyse the variation of this important numerical invariant with the parameters of the system. This procedure allows us to distinguish different chaotic scenarios.

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*Proceedings of the
9th International
Conference on
Difference Equations
and Discrete
Dynamical Systems
(University of Southern
California), Los
Angeles (USA), 2-7
August 2004 (Pub.
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INTRODUÇÃO AO MÉTODO DOS ELEMENTOS FINITOS

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Com esta introdução aos elementos finitos pretendemos apresentar as noções básicas e fundamentais deste método, tanto do ponto de vista teórico (existência e unicidade da solução, convergência), como pratico (calculo explícito de uma aproximação com um computador). Mostramos neste documento o processo completo de implementação que vai desde a modelação matemática de um problema real até à resolução numérica do problema aproximado. Podemos dividir este processo nas etapas: de modelação do problema em equações (capítulo 1); de estudo teórico das equações (capítulos 3 e 7), da discretização das equações e o estudo dos métodos numéricos (capítulos 4 e 8) e finalmente o calculo explícito de uma aproximação (capítulo 5 e 9).

Neste manual, introduzimos as ferramentas usuais dos elementos finitos: problema variacional, teorema de Lax-Milgram e de Lions, princípio do máximo, espaço de discretização finito, os esquemas em espaço e tempo, a estabilidade dos métodos e ordens de convergência do método.

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*Departamento de
Matemática –
Universidade de
Aveiro, Outubro 2005*

BOUNDARY VALUE PROBLEMS AND INTEGRAL RELATIONS IN THE CONTINUUM THEORY OF NEMATIC LIQUID CRYSTALS

Pereira, Pedro Jorge da Silva

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*Imperial College of
Science, Technology
and Medicine,
University of London,
Tese de Doutoramento
em Matemática,
London, United
Kingdom, Outubro de
2005*

Some boundary value problems and integral relations in the continuum theory of nematic liquid crystals are considered. These boundary value problems include the flow of a nematic liquid crystal near the leading edge of an infinite prism as well as the orientational director effects in nematics with small Ericksen number. Reciprocal and related theorems for nematic liquid crystals are also investigated.

In the first boundary value problem, flow of a nematic liquid crystal in an infinite wedge bounded by sidewalls $\theta = \pm\alpha$ (with no-slip condition) is investigated. The fluid is contained in the region $0 \leq r < +\infty$, $-\alpha \leq \theta \leq \alpha$, and $-\infty < z < +\infty$ ($0 \leq \alpha \leq \pi$). The near tip velocity field is assumed to have the form $v_i(r, \theta) = r^\lambda F_i(\theta)$ ($i = r, \theta, z$) as r tends to zero. We investigate the dependence of eigenvalues λ and functions $F_i(\theta)$ on the tilt angle, $G(\theta)$, between the director field and the plane $z = c$ ($c \in \mathbb{R}$) and on the included angle 2α of the wedge shaped prism. In general, when $0 < G(\theta) < \pi/2$ eddies are not found. However, if we impose an appropriate behaviour on the far velocity field so it is orthogonal to the eigenvectors associated with the first real eigenvalues, the remaining flow fields may display eddies.

In the second boundary value problem, orientational director effects in nematic liquid crystals with small Ericksen number are investigated. A moving plate advancing into a sample of nematic liquid crystal is considered. The resulting equations are a system of non-linear partial differential equations for a nematic in the one elastic constant approximation. These equations are reduced to a coupled set of non-linear ordinary differential equations by a suitable transformation. No such transformation seems possible for the many elastic constant case. The resulting equations are solved by analytical methods and strict bounding solutions obtained. These analytical solutions are compared with numerical solutions obtained from the method of successive approximations (Picard iteration method). It is shown using maximum and minimum principles for differential equations that the exact twist and tilt angle solution lies somewhere between the lower and upper strict bounding solutions. Decreasing and increasing recursive sequences of iterated functions are proposed to improve at each

iteration the lower and upper strict bounding solutions. Reciprocal and related theorems are considered for uniaxial and biaxial nematic liquid crystals. In the general case, where the directors of real and reciprocal materials are assumed to coincide, integral relations between velocity and stress fields of the real and reciprocal materials are obtained. Simplified expressions are also obtained for the high viscosity and elasticity limits.