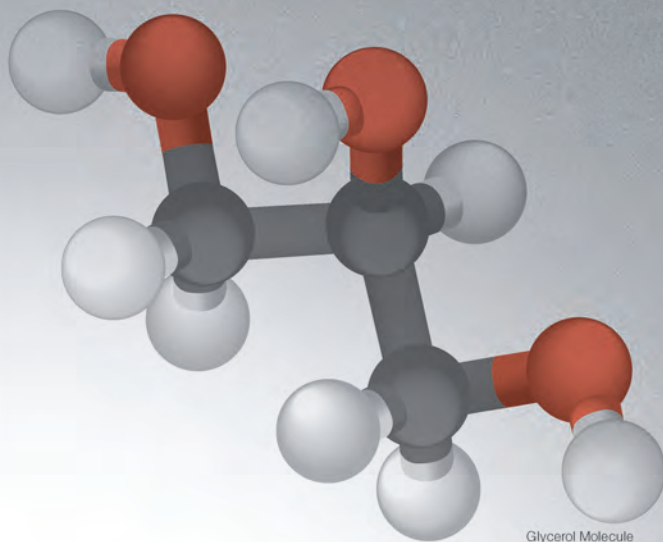


ANNUAL ACTIVITY REPORT 2009



National Institute of
Science and Technology for
Energy & Environment



Annual Activity Report 2009 - INCT-E&A

EXPEDIENT

Editors	Jailson Bittencourt de Andrade (UFBA) Leonardo Sena Gomes Teixeira (UFBA) Lílian Lefol Nani Guarieiro (UFBA)
Proofreader	Jailson Bittencourt de Andrade (UFBA) Leonardo Sena Gomes Teixeira (UFBA) Lílian Lefol Nani Guarieiro (UFBA) Pedro Afonso de Paula Pereira (UFBA) Stelyus Lazaro Mkoma (UFBA)
Production	Editora Cubo
Management	Rafael Mozeto and Larissa Orlandi

Instituto Nacional de Ciência e Tecnologia de Energia e Ambiente (INCT-E&A)

Headquarters	Universidade Federal da Bahia Centro Interdisciplinar de Energia e Ambiente Rua Barão de Jeremoabo, S/N - Ondina CEP: 40170115 Salvador – Bahia
Telephone	+55 71 3283 6821
Home Page	www.inct.cienam.ufba.br

Management Committee

Coordinator	Jailson Bittencourt de Andrade (UFBA)
Vice-Coordinator	Ednildo Andrade Torres (UFBA)

Support



inct
institutos nacionais
de ciência e tecnologia



CNPq
Conselho Nacional de Desenvolvimento
Científico e Tecnológico



C A P E S



fapesb
Fundação de Amparo
à Pesquisa do Estado da Bahia



Ciência e Tecnologia
Ministério da Ciência e Tecnologia

Collaborations



Marinha do Brasil

Braskem

BR PETROBRAS

FAFEN



FINEP
Financiadora de Estudos e Projetos

Production

editora cubo
soluções para o universo acadêmico

Cataloguing Card

Instituto Nacional de Ciência e Tecnologia de Energia Ambiental
(INCT-E&A)

Annual Activity Report / Instituto Nacional de Ciência e Tecnologia
de Energia Ambiental (INCT-E&A). – 2009– . – São Carlos: Editora Cubo,
2009–.

80 p.
ISSN 2178-7891

1. Vehicular emissions. 2. Environmental impacts. 3. Biofuels.
4. Biomass. 5. Fuel mixtures. I. Título.

ANNUAL
ACTIVITY
REPORT
2009



National Institute of
Science and Technology for
Energy & Environment





↓ SUMMARY

MESSAGE OF COORDINATOR 4

INTRODUCTION 6

SCIENCE HIGHLIGHTS 14

FACTS AND FIGURES 66

MAIN EVENTS 68

PUBLICATION 76

ASSOCIATED PROJECT 80



MESSAGE OF COORDINATOR



Energy and Environment are the two greatest challenges of humanity today. In addition to its intrinsic importance, these challenges are directly related to the production of food, the sustainable use of water bodies, and the wealth/poverty of nations. To address the emerging challenges, it is necessary to unify **science** and **education**, an essential condition for the radical transformation of scientific education, from the elementary school to graduate studies. The convergence of scientific disciplines and research fields, historically separated, can not occur without the emergence of new professionals and scientists who recognize the depth of the multifaceted scientific and technological challenges and how smart will be the effort necessary to integrate them. In this sense, the construction of new curricula, new

structures and new educational paths that seek intellectual coherence will be necessary. In this new scenario, innovation emerges as the main fuel for the longevity of the corporation.

Modifying the disciplinary conventional vision in both Scientific and Professional training and in the Activities of Science, Technology and Innovation, involves a conceptual and institutional reformulation, because the departmental configuration reflects the current departmental division. Therefore, we need to advance towards a system with a focus beyond the academic departments, which include “**Structures of Excellence**”, like Institutes, Nucleus, Centers, etc., where the multi- and interdisciplinary approach predominate. In these environments, students must be trained with depth and scope to enable



them to overcome the border of disciplines and sub-areas concerned that enable them to act in an interdisciplinary way. Hence, the development of undergraduate projects, with scientific initiation, or graduate projects should occur, under the supervision of more than one advisor, allowing the training of students seeking a professional environment in which the actions and work in a network of interdisciplinary teams are increasingly encouraged and required. To this end, “**Structures of Excellence**” must have: i) Institutional autonomy, ii) Financial sustainability, iii) Intelligence and leadership, iv) Partnerships with the public and private sectors, v) national and international partnerships, vi) an interdisciplinary research agenda, vii) basic and applied research.

In this sense, the Ministry of Science and Technology’s **PROGRAM FOR NATIONAL INSTITUTES OF C & T, INCT**, could make it

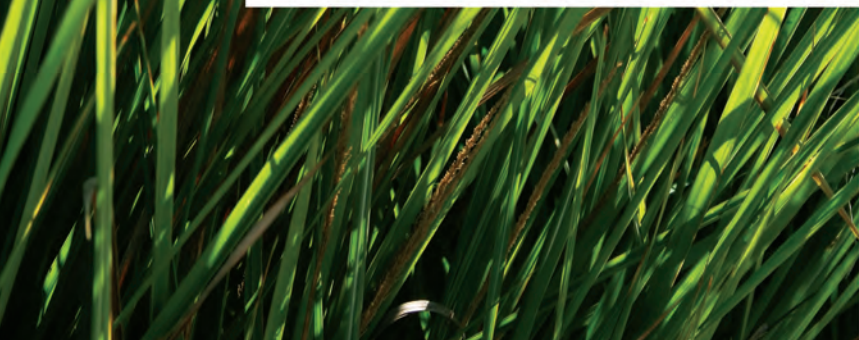
feasible to create the **National Institute for Energy and Environment**, focused on major scientific and technological challenges and, especially, in the training of highly qualified human resources.

The research focus of the National Institute of Science and Technology for Energy and Environment involves the preparation of biofuels, coupled with the recovery of the by-products, formulation and certification of fuels and mixtures of fossil fuels and biofuels; combustion engines testing using bench and chassis dynamometers, and the impact of gases and particulate matter, at the nano- and sub-micron size scales, which are emitted to the atmosphere of urban Brazilian centers. The synergy of research actions, mobility of staff, integration in the training of human resources and the ability to transfer knowledge to society, government and businesses, are the main stock amalgamators of this new INCT – E&A.



Jaílson B. de Andrade
Coordinator

INTRODUCTION



NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY FOR ENERGY & ENVIRONMENT

INSTITUTO NACIONAL DE CIÊNCIA E TECNOLOGIA DE ENERGIA E AMBIENTE (INCT – E&A)

THE INSTITUTE

The headquartered of National Institute of Energy and Environment (INCT-E&A) - CIEnAm is located at the Interdisciplinary Center for Energy and Environment (CIEnAN), Federal University of Bahia. The INCT was founded in 2003 and is involved in Teaching, Research, Extension and Innovation skills oriented for the formation of qualified human resources and the generation of knowledge and technological products in the following areas: i) optimization and eco-efficient energy use, ii) fossil fuels from biomass, iii) Environmental impacts in the atmosphere, lithosphere, hydrosphere and biosphere, iv) Clean technologies, v) Nanotechnology and new materials, and vi) the regulation and management. The *INCT-E&A* acts as a national network of research groups belonging to different states in different Brazilian geographical regions. There is a cooperation within the network in the preparation of biofuels linked to valuation of their by-products, the formulation and certification of either fuels or fuel mixtures (fossil fuel and biofuels), the fuel combustion in engines tested in stationary and roller dynamometer, and the impact of gases and particulate matter (both in micrometer and nanometer scale) emitted to urban atmosphere in Brazil. INCT-E&A's studies also include the life cycle in fuel production with emphasis on carbon sequestration and conversion, impact and toxicology.

RESEARCHERS

The National Institute for Energy and Environment, involves 59 researchers from 39 research groups in 10 different institutions: UFBA,

UFSC, UFRGS, USP, UFRJ, UEL, UNEB, UESB, UEFS and UFPR. Among the 59 researchers, 26 are fellows from CNPq research productivity at level I and 16 at level II. The INCT-E&A involves 50 undergraduate students, 80 masters students and 75 doctorate students. The research groups are involved in carrying out leading-edge research of high quality and internationally competitive in their skills. Thus, the synergy of action research, mobility of personnel, the integration of human resource training and the ability to transfer knowledge to society, government and business are major amalgamators shares of this Institute.

OUR MISSION AND AIMS

This project proposes the preparation of biofuels, coupled with the enhancement of co-products, formulation and certification fuels and mixtures of fossil fuels and biofuels, the combustion stationary engines and dynamometer rollers and the impact of gases and particulate matter (In micrometer and nanometer scale) emitted in the atmosphere of Brazilian urban centers with follow aims:

- To explore oilseeds - To investigate the occurrence and population distributions of oilseed plant species;
- Transesterification and development of new catalysts - Develop new
- heterogeneous catalysts for the reactions of microbiological transesterification;
- To formulate new additives - to formulat and characterize additives for mixtures of diesel, biodiesel and ethanol;
- To Analyze and specify the raw materials, biodiesel and coproducts – Validate and implement analytical methods for

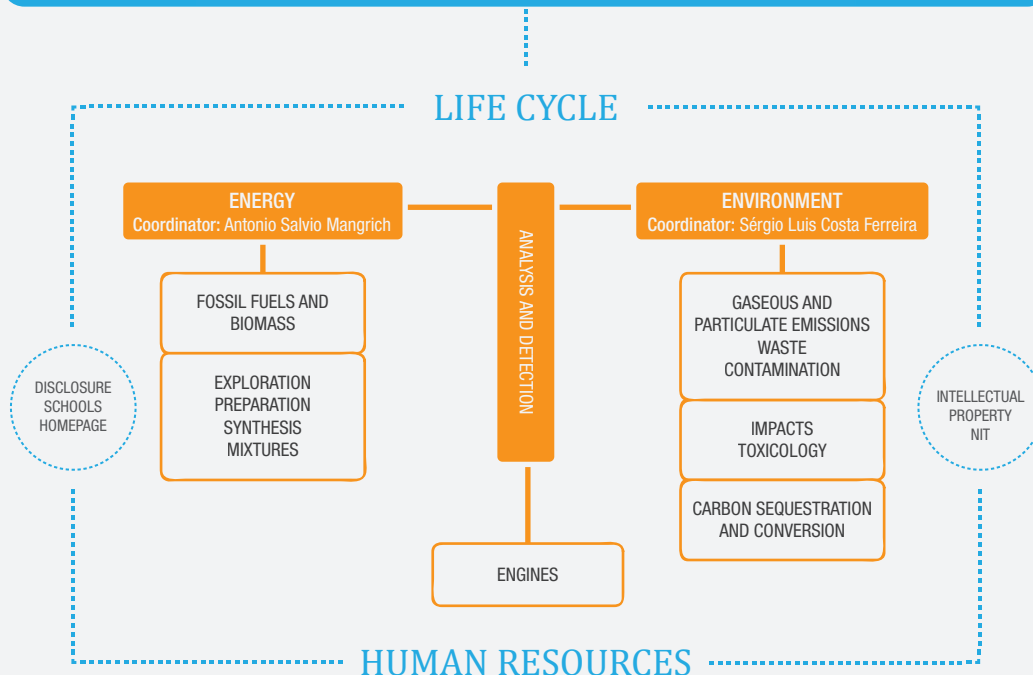
characterization of biodiesel according to legislation;

- To study diesel, ethanol and biodiesel mixtures – preparation of diesel, ethanol and biodiesel mixtures for use in diesel engine testing;
- To use diesel, ethanol and biodiesel in diesel engines - to determine the physico-chemical properties of biodiesel and additives, to study issues from coal combustion and engine

wear and its components, using mixtures, determine;

- To characterize and compare the emissions from fuels - Characterize and evaluate the impacts on the environment from emissions vehicular;
- To study new uses for glycerin – Produce high-value substances aggregate, from changes of glycerol, using the principles of Green Chemistry;

INCT-EA MANAGEMENT COMMITTEE



- To Analyze the biodiesel life cycle - survey the consumption and energy production and environmental impacts at different life cycle stages of the biodiesel production chain.

RESULTS AND PERSPECTIVES

The already obtained results represent a significant contribution of the INCT-E&A's theme which are published in peer reviewed journals. The focus on technology and innovation is reflected on patents, incubated companies working in the technological appropriation of the INCT-E&A's results and the significant number of both small and large companies* that holds scientific and technological cooperation at the Institute. Also, a pilot plant was designed, built, and is operating at present with a production capacity of 5 million L year⁻¹ of biodiesel.

- The continuous training of qualified human resources is one of the primary aims of the INCT-E&A and is reflected in the significant number of undergraduate students, MSc, PhD and post-doc students. The diffusion of science for the society has an important role in INCT-E&A and has several regular activities, as for

example: “*Escolas de Verão e Inverno*” (Summer and Winter Schools), involving about 300 students and professionals in each of them; the Program “*o Cientista Volta à Escola*”, which creates and keeps an interaction between scientists and elementary and middle school teachers and students; and the creation of the “*Química Nova Interativa*” (<http://qnint.sbq.org.br/qni>), a website of Sociedade Brasileira de Química (Brazilian Chemical Society) with an active participation of the INCT-E&A.

- The INCT-E&A has maintained cooperation with the INCT-NAIRA and strong links with others INCTs as *INOMAT*, *INOFA*, *INCT-TMCOcean*, *INCT de Controle Biorracional de Insetos e Pragas*, which take part of a group called “I5+”, that was created at a meeting of the five INCT's, which occurred in November of 2009 in Itaparica, Bahia. At the *Universidade Federal da Bahia*, the INCT-E&A works in conjunction with the INCT-GP. In May 2010 both Institutes had proposed the creation of a new Unity in the UFBA called “*Instituto de Ciência, Tecnologia e Inovação em Energia e Ambiente (ICTI-EA)*”.

See more at: www.inct.cienam.ufba.br

* Petrobrás, Políteno, Braskem, Bahiagásin, Quimis, EBDA (Empresa Baiana de Desenvolvimento Agrícola, Ourofino Agronegócios Agropecuário), Quattor, Biocapital, Evonik, CBMM, Oxiteno, Analytik Jena AG, Jena, Alemanha, Instituto de Tecnologia do Paraná (Tecpar), National Research Center Canada (NRCC) e as empresas incubadas: E&A Energia e Ambiente e Solar Engenharia Sustentável



INCT-E&A'S RESEARCHERS

Adilson José Curtius (UFSC)

CV: <http://lattes.cnpq.br/4423660932752146>

Alexsandro Branco (UEFS)

CV: <http://lattes.cnpq.br/3477981724349561>

Antonio Salvio Mangrich (UFPR)

CV: <http://lattes.cnpq.br/3935366222752874>

Anderson Santos Souza (UFBA)

CV: <http://lattes.cnpq.br/1799081227613161>

Artur J. Santos Mascarenhas (UFBA)

CV: <http://lattes.cnpq.br/3786427643151229>

Asher Kiperstok (UFBA)

CV: <http://lattes.cnpq.br/3733846364293441>

Bernhard Welz (UFSC)

CV: <http://lattes.cnpq.br/5582765254731004>

Caio Mário Castro de Castilho (UFBA)

CV: <http://lattes.cnpq.br/5927149543717327>

Cesário F. das Virgens (UNEB)

CV: <http://lattes.cnpq.br/6089875159011042>

Cláudia Rocha Martins (UFBA)

CV: <http://lattes.cnpq.br/2266319544784610>

Claudio Jose de Araujo Mota (UFRJ)

CV: <http://lattes.cnpq.br/4303587017025599>

Cristina M. A. L. T. M. H. Quintella (UFBA)

CV: <http://lattes.cnpq.br/7897779819494573>

Ednildo Andrade Torres (UFBA)

CV: <http://lattes.cnpq.br/2483185411923070>

Elina Bastos Caramão (UFRGS)

CV: <http://lattes.cnpq.br/0542856843670457>

Gilmara Gonzaga Pedrosa (UFPE)

CV: <http://lattes.cnpq.br/0828599421701934>

Gisele Olímpio da Rocha (UFBA)

CV: <http://lattes.cnpq.br/7767998250007993>

Fábio Alan Carqueija Amorim (UFBA)

CV: <http://lattes.cnpq.br/7583976864322053>

Fernando de Brito Mota (UFBA)

CV: <http://lattes.cnpq.br/6888892134532265>

Francisco C. Rocha de Barros Jr. (UFBA)

CV: <http://lattes.cnpq.br/1085274416109765>

Heloysa M. Carvalho Andrade (UFBA)

CV: <http://lattes.cnpq.br/7228906971455111>

Jailson B. de Andrade (UFBA)

CV: <http://lattes.cnpq.br/4049958660392553>

Jorge Mauricio David (UFBA)

CV: <http://lattes.cnpq.br/8897713171950671>

Juceni Pereira de Lima David (UFBA)

CV: <http://lattes.cnpq.br/0491600109519083>

Leonardo Sena Gomes Teixeira (UFBA)

CV: <http://lattes.cnpq.br/5061261000226463>

Luciana Almeida da Silva (UFBA)

CV: <http://lattes.cnpq.br/8485782557248922>

Luiz Pereira Ramos (UFPR)

CV: <http://lattes.cnpq.br/0721743417678801>

Luiz Souza Carvalho (UFBA)

CV: <http://lattes.cnpq.br/7709656917777783>

Márcia Messias da Silva (UFRGS)

CV: <http://lattes.cnpq.br/7411928094210109>

Marcelo Embiruçu de Souza (UFBA)

CV: <http://lattes.cnpq.br/8281601894113525>

Marcos De Almeida Bezerra (UESB)

CV: <http://lattes.cnpq.br/0914904378670435>

Marcus Vinicius Bahia (UFBA)

CV: <http://lattes.cnpq.br/7490170633207348>

Maria das Gracias Andrade Korn

CV: <http://lattes.cnpq.br/5329137760546794>

Maria Cristina Solci (UEL)

CV: <http://lattes.cnpq.br/7275459975924414>

Maria Goreti Rodrigues Vale (UFRGS)

CV: <http://lattes.cnpq.br/3871635037264920>

Marilena Meira (UFBA)

CV: <http://lattes.cnpq.br/4024570774679705>

Márcia Messias da Silva (UFRGS)

CV: <http://lattes.cnpq.br/7411928094210109>

Marta V. A. Santana de Andrade (UNEB)

CV: <http://lattes.cnpq.br/5757831298712308>

Martha T. P. de Oliveira Castro (UFBA)

CV: <http://lattes.cnpq.br/7713033610492381>

Mauricio Moraes Victor (UFBA)

CV: <http://lattes.cnpq.br/7610291615437934>

Mauro Korn (UNEB)

CV: <http://lattes.cnpq.br/3772927258951858>

Odair Donizeti Leite (UFBA)

CV: <http://lattes.cnpq.br/8436215509083608>

Pedro Afonso de Paula Pereira (UFBA)

CV: <http://lattes.cnpq.br/1073307881297127>

Pedro Ramos da Costa Neto (UTFPR)

CV: <http://lattes.cnpq.br/9194471940037554>

Pérola de Castro Vasconcellos (USP)

CV: <http://lattes.cnpq.br/8971623116160175>

Regina Terumi Yamaki (UESB)

CV: <http://lattes.cnpq.br/3187814947764753>

Ricardo de Araujo Kalid (UFBA)

CV: <http://lattes.cnpq.br/2562159376424787>

Ricardo Lima Guimarães (UFPE)

CV: <http://lattes.cnpq.br/8569508557507316>

Rosana L. Fialho Vieira de Melo (UFBA)

CV: <http://lattes.cnpq.br/8528111459865939>

Sérgio Luis Costa Ferreira (UFBA)

CV: <http://lattes.cnpq.br/9198426685541534>

Silvio A. Beisl Vieira de Melo (UFBA)

CV: <http://lattes.cnpq.br/9170893104155674>

Silvio do Desterro Cunha (UFBA)

CV: <http://lattes.cnpq.br/5661286013847300>

Suzana Modesto de O. Brito (UEFS)

CV: <http://lattes.cnpq.br/7730440304392983>

Valdeilson Souza Braga (UFBA)

CV: <http://lattes.cnpq.br/2198420901829162>

Valéria Belli Riatto (UFBA)

CV: <http://lattes.cnpq.br/9303341278629652>

Valfredo Azevedo Lemos (UESB)

CV: <http://lattes.cnpq.br/6842729418746590>

Vanessa Hatje (UFBA)

CV: <http://lattes.cnpq.br/4132400977039625>

Vilma Mota da Silva (UFBA)

CV: <http://lattes.cnpq.br/6882775610830283>

Walter Nei Lopes dos Santos (UNEB)

CV: <http://lattes.cnpq.br/9064269830700066>

Wilson Araújo Lopes (UFBA)

CV: <http://lattes.cnpq.br/0954702216542832>



1. Universidade Estadual de Feira de Santana - UEFS

Departamento de Química

LABORATÓRIO DE CATALISE E ADSORÇÃO
Leader: Suzana Modesto de Oliveira Brito

LABORATÓRIO DE FITOQUÍMICA
Leader: Alexandro Branco



2. Universidade do Estado da Bahia - UNEB

Departamento de Ciências Exatas e da Terra

GRUPO DE DESENVOLVIMENTO DE SISTEMAS E PROCESSOS DE ANÁLISE QUÍMICA
Leaders: Mauro Korn and Marta Valéria Almeida Santana de Andrade

GRUPO DE PESQUISA E DESENVOLVIMENTO EM QUÍMICA ANALÍTICA
Leaders: Walter Nel Lopes dos Santos and Cesário Francisco das Virgens

NUCLEO DE PESQUISA EM CATALISE HETEROGÊNEA
Leader: Cesário Francisco das Virgens

GRUPO DE PESQUISA EM QUÍMICA ANALÍTICA E AMBIENTAL
Leaders: Madison de Godoi Pereira and Marta V. Almeida Santana de Andrade



3. Universidade Federal da Bahia - UFBA

Campus Anísio Teixeira

QUÍMICA AMBIENTAL E DE MATÉRIAS-PRIMAS ALIMENTARES
Leader: Anderson Santos Souza

Campus Barreiras

Instituto de Ciências Ambientais e Desenvolvimento

QUÍMICA AMBIENTAL E DESENVOLVIMENTO SUSTENTÁVEL
Leader: Oldair Donizeti Leite

Campus Salvador - Executora

Instituto de Química
Centro Interdisciplinar de Energia e Ambiente
Escola Politécnica
Instituto de Física
Instituto de Biologia
Departamento de Zoologia

LABORATÓRIO DE PESQUISA E DESENVOLVIMENTO E QUÍMICA
Leaders: Jailson Bittencourt de Andrade and Pedro A. de Paula Pereira

LABORATÓRIO DE ENERGIA E GÁS
Leader: Ednilde Andrade Torres

GRUPO DE PESQUISA EM QUÍMICA E QUIMIOMETRIA
Leader: Sérgio Luis Costa Ferreira

GRUPO DE PESQUISA EM QUÍMICA ANALÍTICA
Leader: Maria das Graças Andrade Korn

GRUPO DE PESQUISA EM SÍNTESE QUÍMICA E BIOTIVIDADE MOLECULAR
Leaders: Silvio do Desterrô Cunha and Maurício Moraes Victor

LABORATÓRIO DE CATALISE E MATERIAS
Leader: Heloysa M. Carvalho Andrade and Artur J. Santos Mascarenhas

GRUPO DE PESQUISA EM QUÍMICA DE PRODUTOS NATURAIS
Leaders: Jorge Maurício David and Juceni Pereira de Lima David

LABORATÓRIO DE CINÉTICA E DINÂMICA MOLECULAR
Leader: Cristina M. Assis Lopes Tavares da Mata Hermida Quintella

GRUPO DE FÍSICA DE SUPERFÍCIES E MATERIAS
Leader: Caio Mário Castro de Castilho

LABORATÓRIO DE PROCESSOS E TECNOLOGIA
Leader: Silvio Alexandre Beisl Vieira de Melo

GRUPO DE MATERIAS FOTOCATALITICOS
Leader: Luciana Almeida da Silva

LABORATÓRIO DE OCEANOGRAFIA QUÍMICA
Leader: Vanessa Hatje

GRUPO DE QUÍMICA AMBIENTAL E DESENVOLVIMENTO SUSTENTÁVEL
Leader: Oldair Donizeti Leite

GRUPO INTERDISCIPLINAR EM PRODUTOS NATURAIS E CIÊNCIAS AMBIENTAIS
Leader: Anderson Santos Souza

GRUPO INTERDISCIPLINAR EM PRODUTOS NATURAIS E CIÊNCIAS AMBIENTAIS
Leader: Gisele D. da Rocha

GRUPO DE INVESTIGAÇÃO, DESENVOLVIMENTO E INOVAÇÃO ANALÍTICAS
Leader: Leonardo Sena Gomes Teixeira

GRUPO DE PESQUISA EM SUBSTÂNCIAS MARINHAS
Leaders: Vilma Mota da Silva and Wilson Araújo Lopes

LABORATÓRIO DE ECOLOGIA MARINHA TROPICAL
Leader: Francisco Carlos Rocha de Barros Junior

TECNOLOGIAS LIMPAS E MINIMIZAÇÃO DE RESÍDUOS
Leaders: Asher Kiperstok and Ricardo de Araújo Kalid



4. Universidade Estadual do Sudoeste da Bahia - UESB

LABORATÓRIO DE QUÍMICA ANALÍTICA
Leader: Valfredo Azevedo Lemos

NUCLEO DE QUÍMICA ANALÍTICA
Leader: Valfredo Azevedo Lemos

BIODIESEL E DESENVOLVIMENTO SUSTENTÁVEL
Leader: Regina Terumi Yamaki

LABORATÓRIO DE QUÍMICA ANALÍTICA
Leader: Regina Terumi Yamaki



5. Universidade Federal do Rio de Janeiro - UFRJ

Instituto de Química

LABORATÓRIO DE REATIVIDADE DE HIDROCARBONETOS E CATALISE ORGÂNICA
Leader: Cláudio José de Araújo Mota



6. Universidade de São Paulo - USP

Instituto de Química

GRUPO DE PESQUISA EM QUÍMICA ATMOSFÉRICA
Leader: Perola de Castro Vasconcelos



7. Universidade Estadual de Londrina - UEL

Departamento de Química

LABORATÓRIO DE ANÁLISE DOS COMPONENTES DO AR
Leader: Maria Cristina Solci

LABORATÓRIO DE ANÁLISES CROMATOGRAFICAS E AMBIENTAIS
Leader: Maria Cristina Solci



8. Universidade Federal do Paraná - UFPR

Departamento de Química

Centro Politécnico

CENTRO DE PESQUISA EM QUÍMICA APLICADA
Leader: Luiz Pereira Ramos

QUÍMICA DE COORDENAÇÃO AMBIENTAL E ESPECTROSCOPIA DE EPR
Leader: Antonio Salvo Mangrich



9. Universidade Federal de Santa Catarina - UFSC

Departamento de Pós-Graduação em Química

GRUPO DE ESPECTROMETRIA ATÔMICA
Leader: Adilson José Curtius



10. Universidade Federal do Rio Grande do Sul - UFRGS

Instituto de Química

LABORATÓRIOS DE QUÍMICA ANALÍTICA E AMBIENTAL
Leader: Elina Bastos Caramão

GRUPO DE PESQUISA EM ANÁLISE DE TRAÇOS
Leaders: Maria Goreti Rodrigues Vale and Marcia Messias da Silva

INCT-EA'S INSTITUTIONS



SCIENCE HIGHLIGHTS



Thematic Research 1:

ENERGY

FOSSIL FUELS AND BIOMASS
EXPLORATION, PREPARATION, SYNTHESIS AND MIXTURES

- 16** EMISSION PROFILE OF 18 CARBONYL COMPOUNDS, CO, CO₂, AND NO_x EMITTED BY A DIESEL ENGINE FUELLED WITH DIESEL AND TERNARY BLENDS CONTAINING DIESEL, ETHANOL AND BIODIESEL OR VEGETABLE OILS
- 19** CATALYTIC CONVERSION OF CHLOROMETHANE TO METHANOL AND DIMETHYL ETHER OVER METAL-EXCHANGED ZEOLITE Y
- 22** EFFICIENCY CONTROL IN A COMMERCIAL COUNTER FLOW WET COOLING TOWER
- 28** OPTICAL PROPERTIES OF COLLOIDS FORMED IN COPPER-TIN SULFATE SOLUTION CONTAINING RHODAMINE B
- 32** SOYBEAN OIL AND BEEF TALLOW ALCOHOLYSIS BY ACID HETEROGENEOUS CATALYSIS
- 36** BEEF TALLOW BIODIESEL PRODUCED IN A PILOT SCALE

Thematic Research 2:

ENVIRONMENT

GASEOUS AND PARTICULATE EMISSIONS, WASTE AND CONTAMINATION
IMPACTS TOXICOLOGY
CARBON SEQUESTRATION AND CONVERSION

- 41** SIMULTANEOUS DETERMINATION OF Cd AND Fe IN BEANS AND SOIL OF DIFFERENT REGIONS OF BRAZIL USING HIGH-RESOLUTION CONTINUUM SOURCE GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY AND DIRECT SOLID SAMPLING
- 45** DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR DETERMINATION OF COBALT IN WATER SAMPLES
- 47** MULTICOMPONENT COUPLING REACTIONS IN THE SYNTHESIS OF THIOSEMICARBAZONES
- 50** LESSONS FROM THE TERRA PRETA DE ÍNDIOS OF THE AMAZON REGION FOR THE UTILIZATION OF CHARCOAL FOR SOIL AMENDMENT
- 52** DETERMINATION OF TRACE ELEMENTS IN CRUDE OIL AND IN BIOLOGICAL AND GEOLOGICAL SAMPLES BY ATOMIC SPECTROMETRY
- 55** QUANTIFICATION AND SOURCE IDENTIFICATION OF ATMOSPHERIC PARTICULATE POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR DRY DEPOSITION FLUXES AT THREE SITES IN SALVADOR BASIN, BRAZIL, IMPACTED BY MOBILE AND STATIONARY SOURCES
- 62** SPEEDING UP HCI EXTRACTIONS BY EMPLOYING ULTRASOUND ENERGY TO EVALUATE TRACE ELEMENTS BIOAVAILABILITY IN SEDIMENTS

EMISSION PROFILE OF 18 CARBONYL COMPOUNDS, CO, CO₂, AND NO_x EMITTED BY A DIESEL ENGINE FUELLED WITH DIESEL AND TERNARY BLENDS CONTAINING DIESEL, ETHANOL AND BIODIESEL OR VEGETABLE OILS**

Lílian Lefol Nani Guarieiro¹, Amanda Figueiredo de Souza¹,
Ednildo Andrade Torres^{2,3,4}, Jailson B. de Andrade^{1,3,4*}

¹Instituto de Química, Universidade Federal da Bahia – UFBA, 40170290 Salvador, BA, Brazil

²Escola Politécnica, Universidade Federal da Bahia – UFBA, 40210-730 Salvador, BA, Brazil

³Centro Interdisciplinar de Energia e Ambiente – CIEnAm, Universidade Federal da Bahia – UFBA, Canela, 40110-040 Salvador, BA, Brazil

⁴INCT de Energia e Ambiente, Universidade Federal da Bahia – UFBA, 40170-290 Salvador, BA, Brazil

*e-mail: jailsong@ufba.br

**see more at: GUARIEIRO, L.L.N., *et al. Atmospheric Environment* 2009, 43, 2754.

The impact of vehicular emissions on air depends, among other factors, on the composition of fuel and the technology used to build the engines^{1,2}. The reduction of vehicular emissions requires changes in the fuel composition, and improving the technologies used in the manufacturing of engines and for the aftertreatment of gases. In general, improvements to diesel engines have targeted not only emission reductions, but also reductions in fuel consumption. However, changes in the fuel composition have been shown to be a more rapid and effective alternative to reduce pollution^{3,4}. Some factors should be taken into consideration when searching for an alternative fuel to be used in diesel engines, such as emissions, fuel stability, availability and its distribution, as

well as its effects on the engine durability⁵. Thus, in this work, 45 fuel blends (Figure 1) were prepared and their stability was evaluated. The following mixtures (v/v/v) were stable for the 90-day period and were used in the emission study: diesel/ethanol – DE (90/10%), diesel/ethanol/soybean biodiesel – DESB (80/15/5%), diesel/ethanol/castor biodiesel – DEAB (80/15/5%), diesel/ethanol/residual biodiesel DERB (80/15/5%), diesel/ethanol/soybean oil DESO (90/7/3%), and diesel/ethanol/castor DEAO oil (90/7/3%). The influences of the engine on regulated and unregulated emissions were investigated at two constant speeds (1800 and 2000 rpm) with varying load levels.

The experiments were performed using an internal combustion engine (Agrale®, Model



Figura 1. Misturas combustíveis preparadas para a avaliação da estabilidade.

M790, 22 kW) mounted on a dynamometer steady, varying the speed rate (1800 and 2000 rpm) and the charge level (0, 5 and 10 kW). The sampling time was 15 min in each mode of engine operation. Emissions of regulated compounds (CO and NO_x) and CO₂ were measured online using a gas analyzer (Telegon TEMPEST – 100). Sampling of carbonyl compounds was performed using two impinger bottles in series filled with 10 mL of 2,4-DNFHi. All samples were taken in triplicate. Analyses were performed on a system of high performance liquid chromatography coupled to a UV-DAD detector (HPLC-UV-DAD, Agilent 1100, 1 max. = 365 nm). The carbonyl were separated on a column of 2.1 × 250 mm C18 LC (5 mm), using as eluent acetonitrile and water in gradient mode. The identification was made by comparison of retention times to that of a standard mixture of CC and quantification by analytical curves with external standardization.

The 18 carbonyl compounds identified and quantified are shown in Figure 2. Formaldehyde, acetaldehyde, acetone, and propionaldehyde were the CC quantified in higher concentration at less (0 kW), middle (5 kW), and high (10 kW) loads for diesel fuel. The increase of the load showed a decrease of CC emissions of the C1–C3 carbonyl compounds, but the C4–C10 compounds showed

an opposite result and similar time profile in the pure diesel emissions. Figure 2 shows the CC emission rate (%) at 1800 rpm without load (0 kW) using fuel blends compared to pure diesel. The addition of 10% ethanol to diesel showed an increase of approximately 17% in the emission of CC. When increasing the proportion to 15% ethanol, an emission rate of CC that is approximately 25% higher than that of diesel is expected. Thus, the addition of biodiesel from castor oil (AB), residual oil (RB), and soybean oil (SB) showed increases in the emission rate by 19, 39.3 and 55.4%, respectively. This means that the addition of AB to ternary mixture helped to reduce the emissions of CC and SB, and RB contributed to an increase in the emission of CC. The AB has a large percentage of the ricinoleic acid ester, which has a hydroxyl radical in carbon 12. The presence of the hydroxyl group may be contributing to more complete burning, reducing the emission of CC. In this manner, when 3% vegetable oils were added to ternary mixture the emission rate was higher for the OS (98%) than for AO (53%). The acrolein emissions found in the ternary mixture were very significant. The pure diesel, DEAO and DESO did not show any acrolein emission. Therefore, the blends DE, DESB, DEAB, and DERB showed concentrations

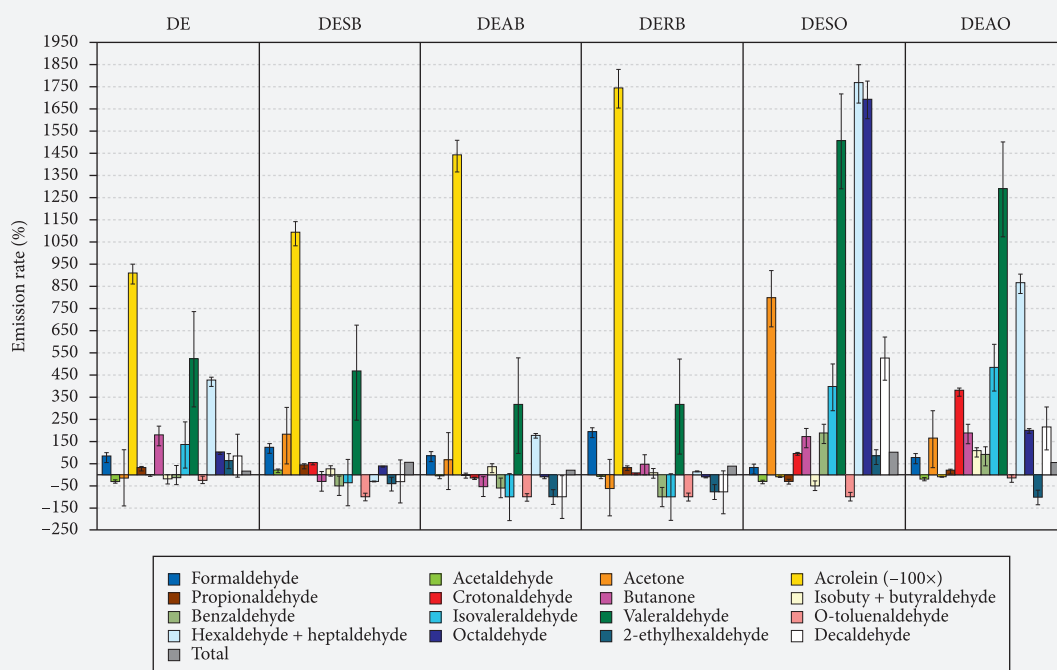


Figura 2. The CC emission rate (%) at 1800 rpm and without load (0 kW) using DE, DEAB, DESB, DERB, DESO, and DEAO fuel blends in comparison to pure diesel.



Figure 3. Diesel engine mounted on a dynamometer steady.

as high as 91.6, 109.8, 144.8, and 175.3 ppbV, respectively, for the engine condition without load at 1800 rpm. The higher part of acrolein emission can be ascribed to total glycerol residue. It was shown before that the RB used in DERB fuel had the higher quantity of total glycerol (0.2988%, w) than the other biodiesels used. This causes DERB to emit more acrolein. Although DESO and DEAO did not emit acrolein, these compounds produced a higher concentration of acetone (4632.6 and 1351.4 ppmV to DESO and DEAO).

The results of this work indicates that NO_x emissions from the fuel blends used (in various operating conditions) decrease 7-75% and 4-85% the emission of NO_x into their rotations in 1800 and 2000 rpm, compared to NO_x emissions for pure diesel. Thus, the addition of oxygenates to diesel

fuel can improve combustion efficiency, resulting in more complete combustion in terms of NO_x .

The addition of 10% ethanol in diesel reduced CO_2 emissions 5-24% (1800 rpm) and 4-6% (2000 rpm), and the presence of co-solvents in the ternary mixture contributed to a further reduction of emissions CO_2 studied only at the higher rotation (2000 rpm). No significant difference was observed in CO, when you use the binary and ternary mixtures. Thus, this research evidence that the use of ternary blends using diesel/ethanol/biodiesel or vegetable oil contributes only in the reduction of NO_x emissions for all engine conditions studied. Thus, with the exception of NO_x , the use of ternary blends results in increased emission rate of the compounds studied.

REFERENCES

1. PINTO, A.C., GUARIEIRO, L.L.N., REZENDE, M.J.C., RIBEIRO, N.M., TORRES, E.A., LOPES, W.A., PEREIRA, P.A.P., ANDRADE, J.B., 2005. Biodiesel: an overview. *Journal Brazilian Chemical Society* 16, 1313-1330.
2. SHI, X., YU, Y., HE, H., SHUAI, S., DONG, H., LI, R., 2008. Combination of biodiesel- ethanol-diesel fuel and SCR catalyst assembly to reduce emissions from a heavy-duty diesel engine. *Journal of Environmental Sciences* 20, 177-182.
3. RIBEIRO, N.M., PINTO, A.C., QUINTELLA, C.M., DA ROCHA, G.O., TEIXEIRA, L.S.G., GUARIEIRO, L.L.N., RANGEL, M.C., VELOSO, M.C.C., REZENDE, M.J.C., DA CRUZ, R.S., OLIVEIRA, A.M., TORRES, E.A., DE ANDRADE, J.B., 2007. The Role of Additives for Diesel and Diesel Blended (Ethanol or Biodiesel) Fuels: A Review. *Energy & Fuels* 21, 2433-2445.
4. DE MENEZES, E.W., DA SILVA, R., CATALUÑA, R. ORTEGA, R.J.C., 2006. Effect of ethers and ether/ethanol additives on the physicochemical properties of diesel fuel and on engine tests. *Fuel* 85, 815-822.
5. GUARIEIRO, L.L.N., PEREIRA, P.A.P., TORRES, E.A., DA ROCHA, G.O., DE ANDRADE, J.B., 2008. Carbonyl compounds emitted by a diesel engine fueled with diesel and biodiesel-diesel blends: sampling optimization and emissions profile. *Atmospheric Environment* 42, 8211-8218.

CATALYTIC CONVERSION OF CHLOROMETHANE TO METHANOL AND DIMETHYL ETHER OVER METAL-EXCHANGED ZEOLITE Y**

Daniella R. Fernandes^{1,2}, Nilton Rosenbach Jr.^{1,2}, Claudio J.A. Mota^{1,2,*}

¹Instituto de Química, Universidade Federal do Rio de Janeiro – UFRJ, Av. Athos da Silveira Ramos 149, CT Bloco A, 21941-909, Rio de Janeiro, Brazil

²INCT de Energia e Ambiente, Universidade Federal do Rio de Janeiro – UFRJ, 21941-909, RJ, Brazil

*e-mail: cmota@iq.ufrj.br

**see more at: FERNANDES, D.R., et al. *Applied Catalysis A: General* 2009, 367, 108.

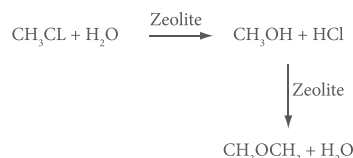
The search for industrial processes of natural gas conversion to liquid fuels and petrochemicals is a major challenge in chemistry. With the increasing price of oil and possible shortage during the 21st century, natural gas appears as a promising raw material, because the world gas reserves exceed the oil reserves¹. As a consequence, natural gas is gaining importance in the world's energetic matrix, motivating the development of new processes, especially concerning the production of clean fuels to improve air quality.

The most common pathway for transforming natural gas is reforming, which produces syngas, a mixture of carbon monoxide and hydrogen². Syngas might then be used in Fischer-Tropsch process³ to produce gasoline and diesel range hydrocarbons, as well as in methanol synthesis, with the use of copper-zinc based catalysts⁴. The main problem associated with natural gas reforming is the high endothermicity of the reaction, which demands a great amount of energy, consequently increasing the operation costs.

On the other hand, halogenation of methane, the main constituent of the natural gas, is a well known reaction. Chlorination is exothermic by 101 kJ/mol, whereas bromination releases 25 kJ/mol of energy. Both reactions can be performed on an industrial scale to produce the halomethane derivatives, either through direct reaction of natural gas with the halogens, or through oxyhalogenation processes, using HCl or HBr and air. In addition, the electrophilic halogenation of methane can be performed with the use of Lewis acid catalysts, yielding monohalomethane derivatives in high selectivity^{5,6}. Thus, development of processes for

halomethane transformation would avoid syngas, and may reduce the economical drawbacks and high energy consumption associated with natural gas transformation.

Methanol is a major commodity, used for production of fuels, petrochemicals and in fuel cell systems⁷. Dimethyl ether (DME) is being considered a clean fuel⁸, and might replace oil in diesel engines, with little or no particulate and sulfur emissions. In the present work we show early results of chloromethane hydrolysis to methanol and DME (scheme 1) catalyzed by metal-exchanged zeolite Y, at mild temperatures and continuous flow conditions.



Scheme 1. Conversion of chloromethane to methanol and dimethyl ether over zeolite catalyst.

The catalytic hydrolysis of chloromethane was carried out in a continuous flow, fixed bed unit, coupled online with a capillary gas chromatograph. The catalyst was firstly pre-treated under flowing nitrogen (40 ml/min) at 773 K for 60 minutes, according to a temperature program (room temperature up to 473 K, remaining at this temperature for 30 minutes and up to 773 K, at 2 K/min). The reactor was then cooled to the reaction temperature and the nitrogen flow was replaced by a flow (40 ml/min) of chloromethane in helium (8 molar%). Water was simultaneously introduced in the reactor by means of a syringe pump. The water/CHCl₃ flow was adjusted to

achieve a molar ratio of 3. An U-tube packed with CaO was placed just after the reactor to trap the HCl formed and the excess water. In control experiments, it was shown that neither chloromethane, nor oxygenated products were significantly adsorbed over the CaO bed at room temperature. Product analyses were carried out in a capillary gas chromatograph using flame ionization detection and a column of DB-624 (cyanopropyl-phenyl-methyl-polysiloxane). The conversion and selectivity were taken from the chromatographic analysis, after correction for the response factors. Blank reactions were carried out replacing the catalyst bed by glass spheres.

Table 1 shows the results of chloromethane hydrolysis at 543 K over all catalysts studied. We chose to compare the catalysts at this temperature to minimize the formation of hydrocarbon by-products, as well as to keep a significant conversion degree. Compared to the blank reaction, all catalysts were active for chloromethane hydrolysis and presented the same conversion range, at approximately the same WHSV. This suggests that the activation step in each zeolite catalyst is similar, probably involving the coordination of chloromethane with the metal cation, and subsequent formation of the adsorbed methoxy group. Neither appreciable deactivation of the catalysts nor selectivity changes were observed during the runs, which normally last 120 minutes.

Methanol was the major product formed on all metal-exchanged zeolite catalysts, with selectivity varying from 76 to 95%. The alkaline metal-exchanged zeolites showed the highest methanol selectivity, in the range of 93 to 95%,

whereas exchange with divalent and trivalent cations decreased the selectivity. The other major product was dimethyl ether (DME), which accounted for 5 to 7% selectivity on alkaline metal-exchanged zeolite Y and 10 to 24% on the MgY, CuY and FeY zeolites. Small hydrocarbons, such as ethene and propene, were also observed over MgY at 543 K.

To get further insight into this possible mechanistic pathway, we performed quantum mechanical calculations. Figure 1 shows the calculated transition state for the methanolysis of an adsorbed methoxy group in the presence of monomeric NaCl, which would be formed upon chloromethane adsorption. The structure of the transition state for hydrolysis (not shown) is similar and involves a calculated activation energy of 15.7 kcal/mol, whereas methanolysis requires an activation barrier of 13.2 kcal/mol, both results computed at

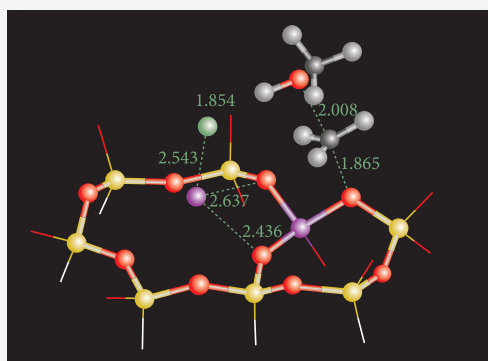


Figure 1. Calculated transition state for methanolysis of an adsorbed methoxy group at ONIOM(PBE1PBE/6-31G(d,p):MND0).

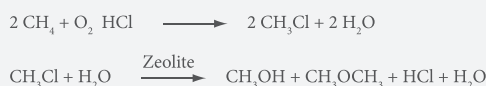
Table 1. Hydrolysis of chloromethane over different metal-exchanged zeolite Y at 543K.

Catalyst	WHSV (h ⁻¹)	Conversion (%)	Selectivity (%)				
			CH ₃ OCH ₃	CH ₃ OH	C ₂ ⁼	C ₃ ⁼	C ₄ ⁺
NaY	10.4	7.0	5	95			
KY	10.3	6.2	7	93			
CsY	10.3	6.3	7	93			
MgY	9.0	5.4	16	76	2	3	3
CuY	8.2	5.0	24	76			
FeY	8.2	8.4	10	90			
Blank	-	0.3	-	100	-	-	-

ONIOM(PBE1PBE/6-31G(*d,p*):MNDO) level of calculation and related to the isolated reactants. The calculations indicated that the methanolysis of the adsorbed methoxy group to afford DME involves a slightly lower energy barrier than hydrolysis to afford methanol. This might explain the formation of DME over metal-exchanged zeolites with little or no Bronsted acidity, like NaY, KY and CsY.

The hydrolysis of chloromethane to methanol and DME can be accomplished in a single step, through the action of metal-exchanged zeolite catalysts. One might argue that this route may have environmental drawbacks, associated with

the release of chlorinated compounds to the atmosphere. Indeed, the HCl produced in the reaction could be used in the oxychlorination of natural gas to chloromethane (scheme 2). Thus, there would be no significant chlorine atom consumption or release to the atmosphere, making the whole process attractive and environmentally clean. Since the oxychlorination is exothermic, the heat produced in the first step might be used in the catalytic hydrolysis, making the whole energy balance attractive with respect to the traditional methanol and DME production from syngas obtained from natural gas reforming.



Scheme 2. Schematic view of the chlorine assisted conversion of methane to methanol/DME. Oxychlorination and catalytic hydrolysis.

REFERENCES

1. LUNSFORD, J.H., 2000. Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century. *Catal. Today* 63, 165-174.
2. ROSS, J.R.H., 2005. Natural gas reforming and CO₂ mitigation. *Catalysis Today* 100, 151-158.
3. de SMIT, E., WECKHUYSEN, B.M., 2008. The renaissance of iron-based Fischer-Tropsch synthesis: on the multifaceted catalyst deactivation behaviour. *Chem. Soc. Rev.* 37, 2758-2781.
4. TIJM, P. J. A., WALLER, F. J., and BROWN, D. M., 2001. Methanol technology developments for the new millennium. *Applied Catalysis A* 221, 275-282.
5. OLAH, G.A., GUPTA, B., FARINA, M., FELBERG, J.D., IP, W.M., HUSAIN, A., KARPELES, R., LAMMERTSMA, K., MELHOTRA, A. K., TRIVED, N. J., 1985. Selective monohalogenation of methane over supported acid or platinum metal catalysts and hydrolysis of methyl halides over γ -alumina-supported metal oxide/hydroxide catalysts. A feasible path for the oxidative conversion of methane into methyl alcohol/dimethyl ether. *J. Am. Chem. Soc.* 107, 7097-7105.
6. BUCSI, I., OLAH, G.A., 1992. Selective monochlorination of methane over solid acid and zeolite catalysts. *Catal. Lett.* 16, 27-38.
7. OLAH, G.A., GOEPPERT, A., PRAKASH, G.K.S., 2006. *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, New York, 2006.
8. SOUSA-AGUIAR, E.F., APPEL, L.G., MOTA, C., 2005. Natural gas chemical transformations: The path to refining in the future. *Catalysis Today* 101, 3-7.

EFFICIENCY CONTROL IN A COMMERCIAL COUNTER FLOW WET COOLING TOWER**

C. A. X. Marques¹; C. H. Fontes¹; R. A. Kalid¹; M. Embiruçu^{1,2,*}

¹Escola Politécnica, Universidade Federal da Bahia, 40210-630 Salvador, BA, Brazil

²INCT de Energia e Ambiente, UFBA, 40170-290 Salvador, BA, Brazil

*e-mail: embirucu@ufba.br

**see more at: Marques, C.A.X., et al. *Energy Conversion and Management* 2009, 50, 2843.

Cooling towers have long been neglected as an important element in the application of eco-efficiency in industrial processes. Given recent concerns about sustainable development, the analysis and implementation of optimization and/or control techniques in cooling towers represent a potential source of improvement in energy efficiency¹ and reduction in water consumption. Cooling towers are much used in process plants and their main process variables, such as the temperature of the water exit stream, the efficiency² and the effectiveness³ are generally not controlled. This is the first work, along of late twenty years, that quantifies the benefits which arise from control improvements in financial terms and therefore shows their economic feasibility because the required instrumentation and controllers are standard.

This work presents closed-loop analysis in a counter flow mechanical draft wet cooling tower of industrial scale capable of operating with a water circulation flow of about 2100 m³/h and coupled with a shell and tube heat exchanger which represents the process thermal demand, as shown in Figure 1a. Three control strategies were evaluated and compared in order to control the performance of the equipment with respect to the eco-efficiency of its operation directly, assuring simultaneously the satisfaction of the process thermal demands.

The phenomenological model adopted to describe the dynamic behavior of the system (Figure 1a) considered as a starting point the works of Majumdar et al.⁴, Younis et al.⁵ and Al-Nimr⁶, and consists of three coupled partial differential equations, two ordinary differential equation and one algebraic equation. The thermodynamic properties considered for the air-water mixture

were obtained from ASHRAE⁷. The model is based on the following assumptions⁸ (Figure 1b shows an idealized model of heat exchange in cooling towers, using thermal resistances):

- The cooling tower operates under adiabatic conditions;
- The water flow changes vertically throughout the tower, remaining constant in each section;
- The density and the specific heat of the water are constant;
- The dry air flow is constant. However, the density and the specific heat of the air change vertically throughout the tower, remaining constant in each section;
- The fill packing is uniformly wet and in thermal equilibrium with the aqueous phase;
- Water waste due to drifting and blow down is negligible;
- The Lewis factor is equal to one;
- There is no meaningful delay between the tower and heat exchanger.

The equations comprise a transient model with distributed parameters (one-dimension). The line method was used in the dynamic systems simulation. The derivatives of position were approximated through finite differences and the time integration was carried out using the Klopfenstein's method. The fill packing volume was divided into 10 sections, leading to a differential algebraic system with 31 ordinary differential equations and 10 algebraic equations.

In the literature, an adjustment of a complete phenomenological model to a counter flow wet cooling tower of industrial scale is not presented. In this work, dynamic data collected during the startup (open-loop and unsteady state conditions) of a commercial cooling tower operating in a cellulose production unit located in Brazil

were used to estimate the model parameters. The estimation procedure was also based on correlations proposed in the literature and in the real operation conditions of the equipment. Figure 1c presents the temperature predicted for the water outlet stream together with the real data. The model provides a good description of the cooling process considering that the profile of the air outlet stream was also satisfactory, lying between the inlet and outlet water temperatures (McKelvey and Brooke, 1959 in Mohiuddin and Kant⁹).

Three control strategies were analyzed and the water and energy consumptions were estimated in each case. The first comprised the adoption of a split-range for the control of the cooling water temperature alone. The second strategy comprised a split-range for the control of tower efficiency. Finally, a combination of override and split-range

control of two performance indices (efficiency and effectiveness) considering a SISO (Single-Input, Single-Output) loop for each controlled variable was used. In each case, simultaneous disturbances in the thermal demand and in the wet bulb temperatures were applied, according to Figures 8a and 8b.

In all cases, the PID tuning parameters were selected through an optimal tuning method, which involved the solution of an optimization problem to minimize the deviations between the controlled variable and its setpoint^{11,13}. This strategy is also adopted in the tuning of a PI-fuzzy control applied to a nylon polymerization semi-batch reactor with variable setpoints for pressure and temperature¹⁴.

The first closed-loop simulation test (strategy I) comprises a regulatory problem in which the setpoint of the cooling water temperature is 30 °C, according to the tower design specification.

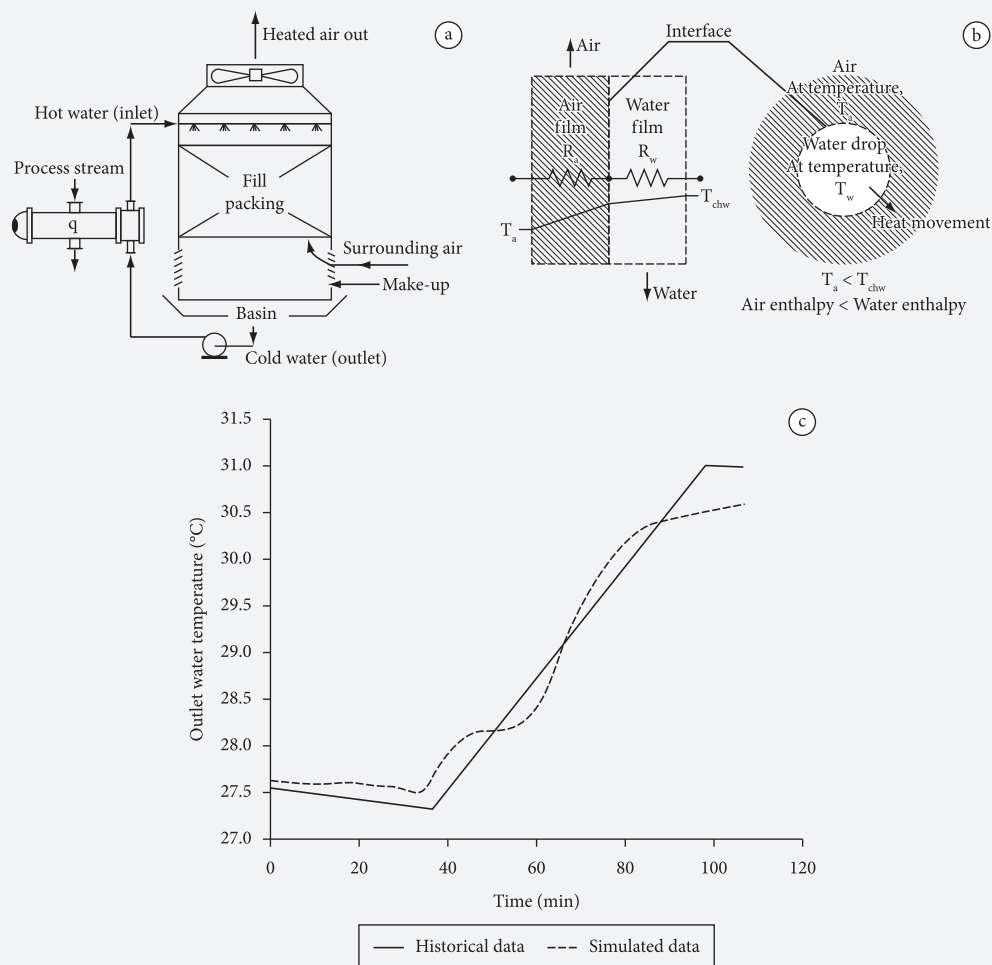


Figure 1. a) Process flowsheet; b) Heat exchange scheme using an electric analogy (based on Guang-Yu Jin et al.¹⁰); c) Outlet water temperature: Simulated and historical data.

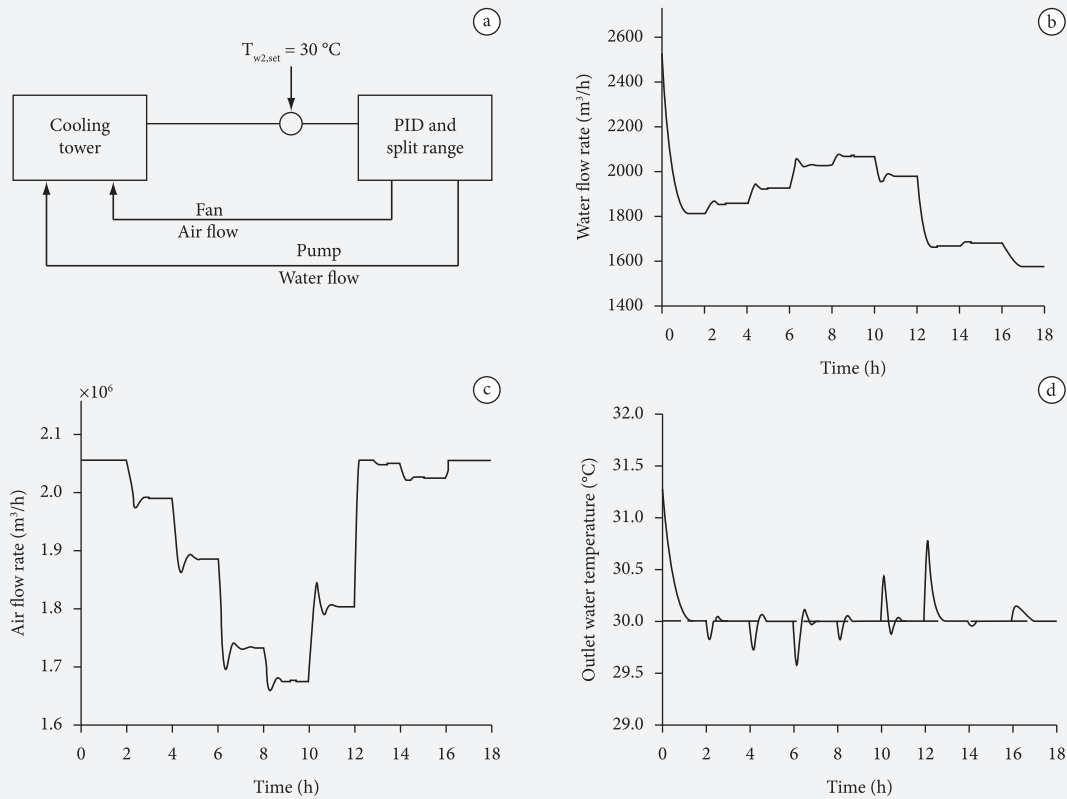


Figure 2. Control strategy I: a) Split-range strategy designed to control outlet water temperature; b) Water flow; c) Air flow; (d) Outlet water temperature.

This split-range range strategy is presented in Figure 2a. Figures 2b and 2c present the behavior of the manipulated variables and Figure 2d shows the behavior of the outlet water temperature. A feasible performance for the manipulated variables can be verified and the control is able to cope with the disturbances to keep the controlled output close to its setpoint. Moreover, it can be seen that all the closed loop tests presented in this work comprise a mixed control problem (regulatory and servo) as the initial conditions of the controlled variables are not equal to the setpoint established in each case.

In the second closed-loop test (strategy II), the efficiency setpoint was assumed to be equal to 80%. Manipulated variables and constraints were the same as strategy I. The diagram of this split-range range strategy is presented in Figure 3a and other tuning parameters were estimated considering this specific control problem. Figure 3b presents the behavior of the controlled variable. It shows that efficiency had not reached its setpoint value and an offset is presented. This can be explained by the physical restrictions of the tower considering that, although the setpoint value is that of the

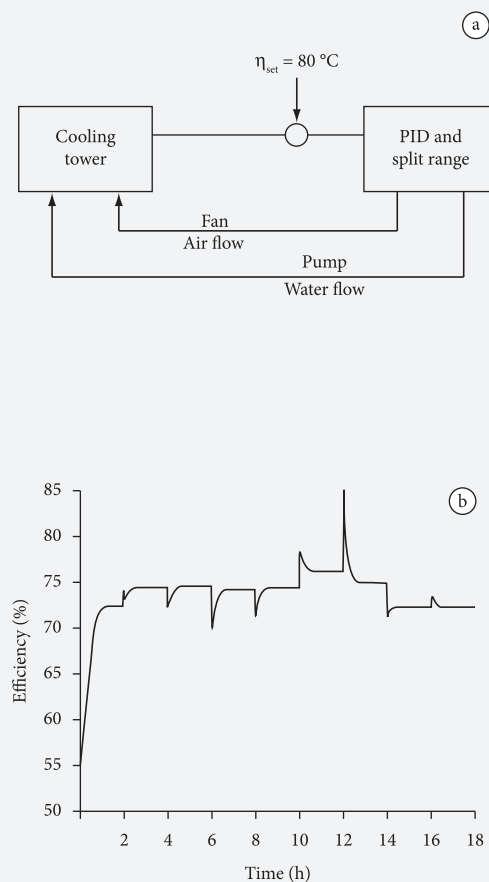


Figure 3. Control strategy II: (a) Split-range strategy designed to control efficiency; (b) Tower efficiency.

design specifications, the parameters of the model that represents the cooling tower were obtained using the process data of a commercial tower which deviates from its design conditions because of aspects such as fouling which have to be taken into consideration over operation time. However, the control strategy is capable of maintaining the efficiency value close to the desired setpoint and, as can be seen in the following section, a notable improvement in tower performance is seen.

The third closed-loop simulation test (strategy III) comprised an override/split-range combination in order to maximize the cooling tower performance through the use of two PID controllers considering simultaneously the control of both efficiency and effectiveness, variables with opposite behaviors as shown earlier. The diagram of this override/split-range strategy is presented in Figure 4a. Here, whenever effectiveness drops below its minimum threshold value (low effectiveness, $\epsilon_l = 70\%$), the control is switched to the PID controller associated to the maximization of the effectiveness. On the other hand, if the effectiveness value reaches its maximum threshold value (high effectiveness, $\epsilon_H = 80\%$), the PID controller associated to the efficiency control is activated. Despite the fact that the air and water flows are manipulated simultaneously through a split-range strategy, the effect of the water flow is more expressive in the efficiency control and the same is valid for the air flow-effectiveness interaction.

Figures 4b and 4c present the behavior of manipulated and controlled variables. Considering the infeasibility of keeping efficiency and effectiveness simultaneously at their setpoints, the override/split-range strategy proposed is capable of monitoring both outputs and to assure the values are maintained within satisfactory levels.

A comparative analysis of all control strategies together with the open-loop performance is presented in Table 1 considering the water and energy consumption obtained for each scenario. This table also presents the variation in the energy and water consumption and the monetary savings resulting from the adoption of the open-loop behavior as reference.

Although control strategy I results in a 0.19% increase in water consumption, which represents approximately 830 m³/year, the overall closed-loop results show a significant reduction in energy and water consumption directly associated to the tower operation (fans and pump). In control strategies II and III where efficiency is directly controlled, reductions of 960 m³/year and 1090 m³/year, respectively, are estimated for water consumption.

The greatest benefit brought about by the control strategies is that of a significant reduction in energy consumption, mainly for strategy II where direct control of the tower efficiency is performed. Considering the results obtained with this control strategy, and based on the price of electric energy in Brazil, an annual energy saving of about US\$ 380,000/year is estimated. Moreover, another important positive environmental impact is also achieved through water savings, although not as important as energy savings from a financial point of view given the current low price of water. The results also suggest that direct control of tower efficiency can be enough to assure the high performance of the towers as well as satisfy process demands. Important environmental positive impacts are obtained through reductions in water and energy consumption.

Table 1. Water and energy consumptions and their variations (%) in relation to the open-loop case over 18 hours of operation

	Strategy I	Strategy II	Strategy III	Open-loop results
Water consumption (m ³)	923.3 (+ 0.19)	919.5 (- 0.22)	919.3 (- 0.25)	921.6
Energy consumption (pump) (kWh)	4268.7 (- 62.2)	2565.7 (- 77.3)	4332.0 (- 61.7)	11297.0
Energy consumption (fans) (kWh)	3035.0 (- 17.3)	3667.1 (- 0.04)	3469.8 (- 5.4)	3668.6
Total energy consumption (kWh)	7303.7 (- 51.2)	6232.8 (- 58.4)	9128.2 (- 39.0)	14966.0
Monetary savings (US\$)	730	840	560	-

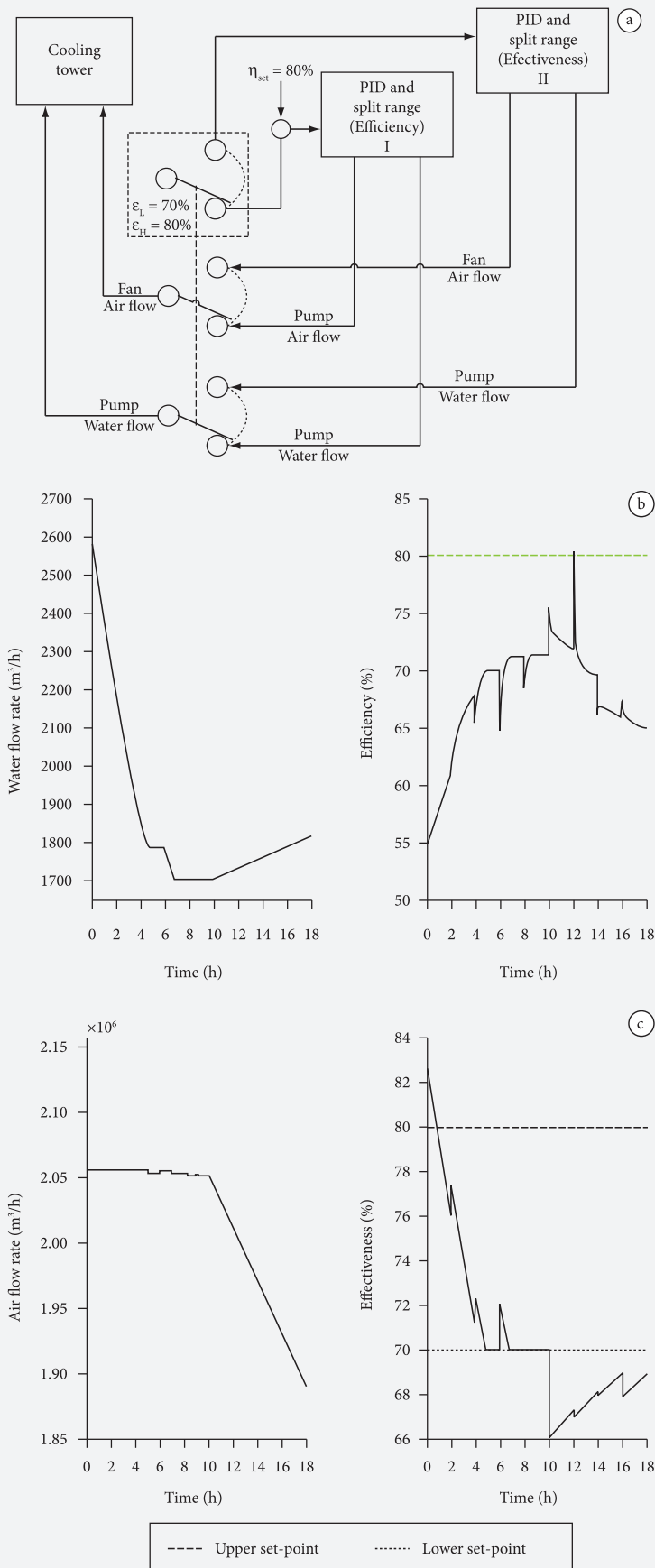


Figure 4. Control strategy III: a) Override/split-range strategy designed to control efficiency and effectiveness; b) Water flow and tower efficiency; c) Air flow and effectiveness.

REFERENCES

1. STOUT JR, M.R., LEACH, J.W., 2001. Cooling tower fan control for energy efficiency, *Journal of Energy Engineering* 99, 7-31.
2. FISENKO, S.P., BRIN, A.A., PETRUCHIK, A.I., 2004. Evaporative cooling of water in a mechanical draft cooling tower. *International Journal of Heat and Mass Transfer*, 47, 165-177.
3. KHAN, J.R., ZUBAIR, S.M., 2001. An improved design and rating analyses of counter flow wet cooling towers. *International Journal of Heat and Mass Transfer* 123, 770-778.
4. MAJUMDAR, A.K., SINGHAL, A.K., SPALDING, D.B., 1983a. Numerical modeling of wet cooling towers – Part 1: Mathematical and physical models, *Journal of Heat Transfer* 105, 736-743.
5. YOUNIS, M.A., FAHIM, M.A., WAKAO, N., 1987. Heat input-response in cooling tower-zeroth moments of temperature variations, *Journal of Chemical Engineering of Japan* 20, 615-618.
6. AL-NIMR, M.A., 1999. Modeling the Dynamic Thermal Behavior of Cooling Towers Containing Packing Materials. *Heat Transfer Engineering* 20, 91-96.
7. ASHRAE - Fundamentals Handbook 2001 (SI Edition), American Society of Heating, Refrigerating and Air-Conditioning Engineers.
8. LEBRUN, J., SILVA, C.A., 2002. Cooling tower - model and experimental validation, *ASHRAE Trans.* 108, 751-759.
9. MOHIUDDIN, A.K.M., KANT, K., 1996. Part I: Selection and tower characteristics, *International Journal of Refrigeration* 19, 43-51.
10. JIN, G., CAI, W. LU, L., LEE, E.L., CHIANG, A., 2006. A simplified modeling of mechanical cooling tower for control and optimization of HVAC systems, *Energy Conversion and Management* 48, 355-365.
11. ALFANO NETO, C., EMBIRUÇU, M., 2000a. Optimization-Based Tuning of PID Controllers. Multi-Loop Systems, *International Congress of Chemical and Process Engineering (CHISA)*, 15p.
12. ALFANO NETO, C., EMBIRUÇU, M., 2000b. Optimization-Based Tuning of PID Controllers. Cascade Systems, *International Congress of Chemical and Process Engineering (CHISA)*, 16p.
13. ALFANO NETO, C., EMBIRUÇU, M., 2000c. Tuning of PID Controllers: an Optimization-Based Method, In *Digital Control 2000: Past, Present and Future of PID Control* (org.: J. Quevedo; T. Escobet), ISBN: 0080436242, 415-420.
14. WAKABAYASHI, C., EMBIRUÇU, M., FONTES, C., KALID, R., 2009. Fuzzy control of a nylon polymerization semi-batch reactor. *Fuzzy Sets and Systems* 160, 537-553.

OPTICAL PROPERTIES OF COLLOIDS FORMED IN COPPER-TIN SULFATE SOLUTION CONTAINING RHODAMINE B**

Tatiana B.F. Guimarães¹, Iuri Pepe³, Antônio Ferreira da Silva³,
Antônio S. Mangrich^{2,3}, Jailson B. de Andrade^{1,2}, Luciana A. Silva^{1,2}

¹Instituto de Química, Universidade Federal da Bahia – UFBA, 40170-290, Salvador, BA, Brazil

²Instituto Nacional de Ciência e Tecnologia, INC&T de Energia e Ambiente, Universidade Federal da Bahia – UFBA, Salvador 40.170-290, Bahia, Brazil

³Instituto de Física, Universidade Federal da Bahia – UFBA, 40170-290, Salvador, BA, Brazil

⁴Departamento de Química, Universidade Federal do Paraná – UFPR, Centro Politécnico, 81531-990 Curitiba, PR, Brazil

*e-mail: las@ufba.br

**see more at: GUIMARÃES, T.B.F., *et al. Journal of Alloys and Compounds* 2009, 481, 654.

Tin dioxide is a typical wide band gap n-type semiconductor (3.6 eV for crystalline SnO₂) and one of the most widely used semiconductor oxides due to its chemical and mechanical stability. It can be used for many applications, such as gas sensors, solar collectors, transparent conductors and others. Recently, one or bi-dimensional structures, such as nanowires and thin films, have attracted increasing attentions, owing to its enhanced surface-to-volume ratio and promising applications for gas sensors and electronic nanodevices.

Traditionally, tin dioxide can be prepared by many different wet chemical methods, such as precipitation, hydrothermal, solvothermal, sol-gel, gel-combustion, spray pyrolysis, polymerized complex and amorphous citrate method. Furthermore, stannic ions in aqueous solution tend to precipitate in finely dispersed tin oxide particles and can lead to sludge formation. Sn(IV) compounds formed by slow oxidation of Sn(II) are capable of forming unstable colloids that coagulate rather quickly, yielding precipitates containing Sn(IV) and Sn(II). Besides, the addition of Sn(IV) into Sn(II) solution containing sulfuric acid results in the formation of yellow-coloured Sn(IV)-Sn(II) colloids. It is a rare case when the same element in two different states can form a sol¹. However, this process can be reversed if Cu²⁺ ions are added to the colloidal suspension, accelerating the Sn(II) oxidation. On the other hand, oxidation inhibitors can be used to maintain the stability of

an acidic tin electrolyte during prolonged storage and processing times. Many antioxidants, such as sodium sulfite, hydrazine, carbohydrazide, methylethylketoxime, hydroquinone and diethylhydroxylamine, are used to reduce the tendency of stannous ions to oxidize in the presence of dissolved oxygen².

We studied the optical characterization of Sn(IV)-Sn(II) colloidal particles formed in sulfuric acid solution containing Sn(II) and Cu(II). In this study, we used sulfur dioxide and Rhodamine B to slow the oxidation of Sn(II) to Sn(IV) and ethanol to control the precipitation. The present study also aimed to determine the composition of the colloidal particles formed.

Figure 1 shows the XRD patterns of the powders obtained from different samples. The peak positions in each sample agree well with the reflections of bulk SnO₂, but the width of the reflections is considerable broadened, indicating low crystallinity, typical of the colloidal systems. However, it was not possible to conclude that RhB was incorporated in the synthesized materials, since no peaks associated with Rhodamine B were observed in the infrared spectra.

The crystallite size of the samples was estimated with the Scherrer's equation:

$$D = \frac{0.89\lambda}{B \cos \theta}$$

where λ is the X-ray wavelength of 1.541 Å, θ is the Bragg diffraction angle and B is the full width at half maximum (FWHM) of θ . Particle sizes vary

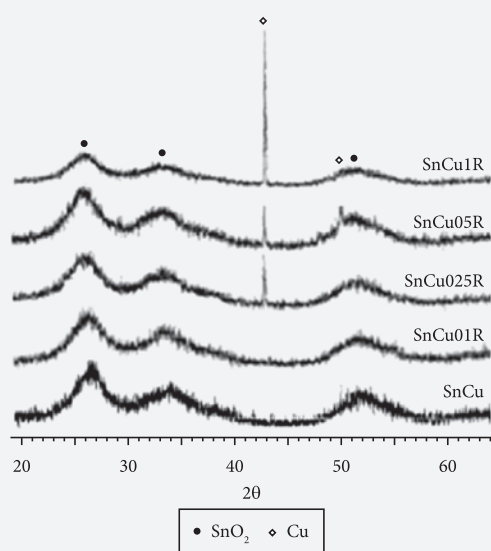


Figure 1. XRD spectra of the samples obtained without (SnCu) and with Rhodamine B: 0,1 (SnCu01R); 0,25 (SnCu025R); 0,5 (SnCu05R); 1,0 (SnCu1R) mL RhB solution.

smoothly with addition of RhB until 0.5 mL, ranged from 5.6 to 7.3 nm. However, a large increase in Cu doping concentration, for addition of 1 mL of RhB solution results in an agglomeration of the small particles, increasing the crystallite size to 280 nm.

For all samples there is no difference among peaks attributed to colloidal SnO₂, indicating that RhB does not affect the colloid crystallinity. For SnCu025R, SnCu05 and SnCu1R samples obtained with the addition of 0.25 mL, 0.50 mL and 1.0 mL of RhB solution, respectively, it is possible to identify peaks attributed to metallic copper. The peaks become narrower and more intense when the amount of RhB solution increases. However, EDX analysis reveals that tin is the major element present in all samples. In terms of metallic elements, the average value of tin in all samples is $98.21 \pm 0.55\%$. Furthermore, the EPR spectra (Figure 2) confirm the presence of copper(II) ion in a predominantly octahedral environment. It can also be noted that no shift in the SnO₂ peak positions or any copper oxides or ternary compounds is observed in the XRD patterns. This leads to the conclusion that doping SnO₂ with Cu²⁺ has occurred. In this case, some Sn⁴⁺ ions are replaced with Cu²⁺ based on the comparable radii of Sn⁴⁺ and Cu²⁺ (69 and 73 pm, respectively).

The EPR spectra (Figure 2) were examined to identify the electronic changes in the copper centers. The EPR spectra of those materials are typical of Cu²⁺ ions in axial symmetry since the Cu²⁺ ions in these compounds are located in octahedral sites surrounded by six oxide ions. The Hamiltonian parameters obtained in the simulations of the EPR spectra suggest that the orbitals of the copper ion underwent a tetragonal distortion due to the elongation in the direction of the z axis. In addition, the values of the $g_{\parallel}/A_{\parallel}$ ratio around, $180 \times 10^{-4} \text{ cm}^{-1}$, for the octahedral sites confirm the surrounding of oxide ions and the tetragonal distortion for those sites³. In the simulation of the EPR spectra of the SnCu01R sample, two spectra were required, since copper can occupy octahedral and tetrahedral sites in copper-doped tin oxide. The simulated spectrum of the SnCu01R is the result of the sum of both the octahedral and tetrahedral spectra. The large EPR line around 310 mT (Figure 3) can represent copper tetrahedral sites also on the other studied samples, but the feature in the high field (350-390 mT) does not confirm this hypothesis⁴.

In our synthesis procedure we used starting solutions containing Cu(II) saturated with SO₂ gas, and the resulting solutions immediately change color from blue to green. This color change is indicative of the formation of Cu(II)-S(IV) complexes. The reduction of Cu(II) by S(IV), in

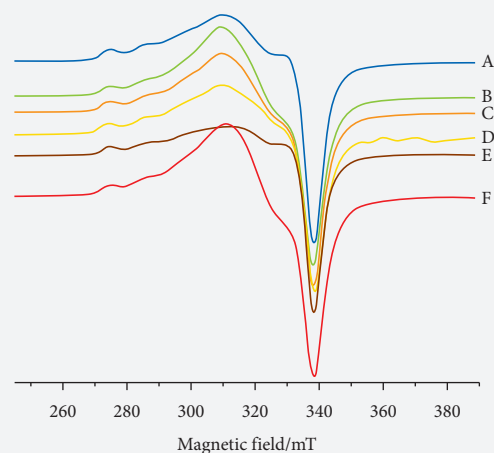


Figure 2. EPR spectra of (A) SnCu, (B) SnCu1R; (C) SnCu05R, (D) SnCu01R; (E) SnCu025R; (F) SnCu2R, taken with powdered samples at liquid nitrogen temperature (77 K).

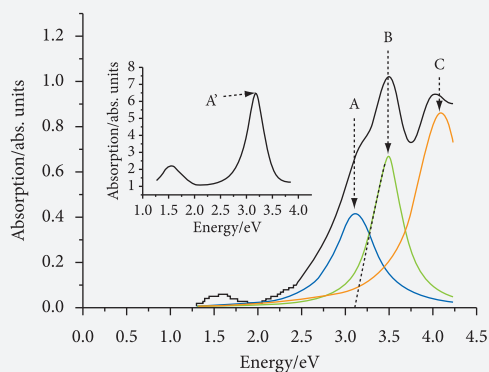
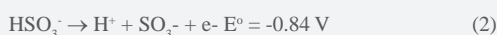
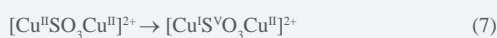
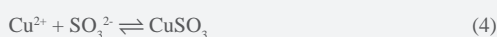
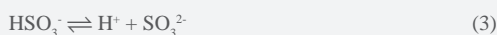


Figure 3. Transmission spectrum of the sample obtained without Rhodamine B. The inset shows the spectrum of a sample obtained with an addition of 1.0 mL of Rhodamine B solution. Peaks: A = 397 nm (3.12 eV); B = 355 nm (3.49 eV); C = 303 nm (4.09 eV) and A' = 392 nm (3.16 eV).

terms of the predominant Cu(II) and S(IV) species, is thermodynamically unfavorable:

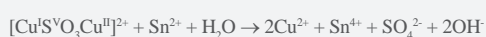


The unfavorable ΔG° for this reaction indicates that other processes must be taken into account. At $\text{pH} < 6.0$, positively charged dimeric Cu(II)-S(IV) complexes are formed upon mixing solutions of Cu(II) and S(IV) as follows:



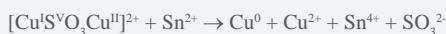
These complexes react to form a mixture of Cu^+ , Cu^{2+} , SO_4^{2-} and SO_3^{2-} in apparent equilibrium with Chevreul's salt ($\text{Cu}_2^{\text{I}}\text{SO}_3 \cdot \text{Cu}^{\text{II}}\text{SO}_3 \cdot 2\text{H}_2\text{O}$). At the pH conditions in our experiments (~1), Chevreul's salt does not precipitate, since the double sulfites series forms only at pH 3. Thus, based on this fact and the FTIR and XRD results, it is reasonable to suggest that the transient complex formed in equation 7 could combine with stannous ions by two pathways:

I. Without Rhodamine B



II. With Rhodamine B

At the same time, in the sulfuric acid media Rhodamine B can easily change, producing a species with a molecular environment similar to an α -hydroxy acid which could mediate the copper disproportionation reaction:



The reaction above may justify the appearance of metallic copper and Cu^{2+} in SnCu025R, SnCu05 and SnCu1R samples prepared with RhB addition. Our findings also suggest that most of the Sn(IV) precipitates as SnO_2 with low crystallinity. FTIR spectra suggest that $\text{Sn}(\text{OH})_2(\text{SO}_4)_2^{2-}$ species formed by partial hydrolysis of stannic ions present in the outer part of the double layer of the sols must be present on the SnO_2 surface.

Figure 3 shows the measured absorption spectrum for SnCu sample as a function of photon energy. It consists of a complex broad band with an abrupt increase in the light transmission at 2.4 eV (520 nm) and a band centered at 1.54 eV (800 nm), typical of Cu^{2+} in octahedral sites distorted by the Jahn-Teller effect. The deconvoluted spectrum at higher energies exhibits three light absorption structures with maximum absorptions at 3.12 eV (397 nm), 3.49 eV (355 nm) and 4.09 eV (303 nm).

The peak centered at 4.09 eV could be attributed to residual copper sulfate remaining from the synthesis procedure, since sulfated samples containing Cu^{2+} exhibit a broad band around 300 nm. In order to explain the second light absorption structure, we invoke the results obtained by Ferreira da Silva et al.⁵ in a previous study of the optical properties of SnO_2 , both theoretical and experimental. In that study, they used a transmission spectroscopy technique, the same apparatus used in the present work, for the measurements of the band gap energy. The authors found an experimental band gap energy of 2.9 eV at room temperature and the corresponding theoretical value 3.4 eV at zero-temperature. We achieve good agreement between this value and the hypothetical band gap energy of the second absorption structure centered at 3.49 eV, determined by geometrical method to be 3.12 +/- 0.09 eV. It could be attributed to un-doped amorphous SnO_2 in a segregated phase. Finally, the band centered at 3.12 eV appears in the spectra of both samples prepared without and with RhB.

The addition of Rhodamine B dramatically influences the spectra profile. One can clearly see only two bands in the spectrum of SnCu1R, shown as the detail in Figure 3. The complex band at higher energies is reduced to one narrow band centered at 3.16 eV, too close to the first band centered at 3.12 eV, and thus resulting in the deconvolution of the SnCu spectrum. On the other hand, Cu²⁺ is still present in an octahedral environment, as attested by the band centered at 1.54 eV. No band associated with Rhodamine B was observed. This evidence leads us to conclude that a new material series with interesting optical properties was obtained. These materials consist of Cu-doped amorphous SnO₂ as predominant base material with Sn(OH)₂(SO₄)₂²⁻ species attached onto the surface.

In order to evaluate the influence of the added amount of Rhodamine B, several spectra were taken from different samples prepared with varying

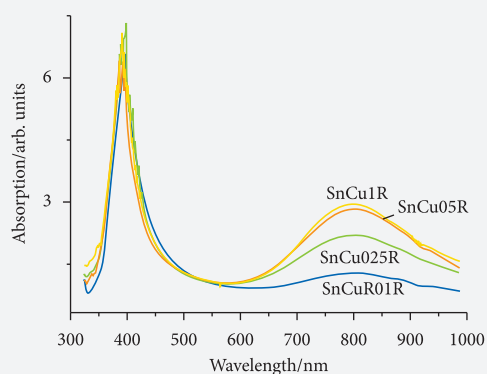


Figure 4. Transmission spectra of the samples obtained with Rhodamine B.

amounts of Rhodamine B solution (Figure 4). A minor amount of RhB, such as 0.1 mL, is enough to yield a change in the spectrum profile when compared to a SnCu sample, but all those samples show quite similar spectra, except for the absorption band intensity centered at 800 nm. The intensity of the absorption is strongly influenced by the amount of Rhodamine B, as can be seen in Figure 4.

Larger volumes of RhB solution increase the absorption intensity at 800 nm, suggesting more Cu²⁺ incorporation. As a consequence, a slight change in the energy at the inflexion point for starting absorption can be observed (Figure 5). For example, an addition of 2 mL of Rhodamine B solution increases the band gap energy by 0.2 eV.

The versatility of these materials is in the possibility of changing the band gap energy, which is useful in many optoelectronic device applications.

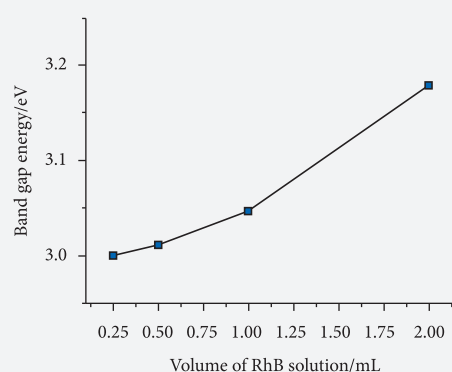


Figure 5. Band gap energies of the samples as a function of the volume added of Rhodamine B solution.

REFERENCES

1. ZHANG, J., GAO, L., 2004. Synthesis and characterization of nanocrystalline tin oxide by sol-gel method. *J. Solid State Chem.* 177, 1425-1430.
2. LOW, C. T. J., WALSH, F. C., 2008. The stability of an acidic tin methanesulfonate electrolyte in the presence of a hydroquinone antioxidant. *Electrochim. Acta* 53, 5280-5286.
3. ARIZAGA, G. G. C., MANGRICH, A. S., WYPYCH, F., 2008. Cu²⁺ ions as a paramagnetic probe to study the surface chemical modification process of layered double hydroxides and hydroxide salts with nitrate and carboxylate anions. *J. Colloid Interface Sci.* 320, 238-244.
4. SILVA, L. A., DE ANDRADE, J. B., MANGRICH, A. S., 2007. Use of Cu²⁺ as a metal ion probe for the EPR study of metal complexation sites in the double sulfite CuI₂SO₃·CdII₂SO₃·2H₂O. *J. Braz. Chem. Soc.*, 18, 607-610.
5. FERREIRA DA SILVA, A., PEPE, I., PERSSON, DE ALMEIDA, C., J. S., ARAÚJO, C. M., AHUJA, R., JOHANSSON, B., GUO, J. H., 2004. Optical properties of oxide compounds PbO, SnO₂ and TiO₂. *Physica Scripta*, T109, 180-183.

SOYBEAN OIL AND BEEF TALLOW ALCOHOLYSIS BY ACID HETEROGENEOUS CATALYSIS**

Rafael Augusto Soldi, Angelo Roberto de Oliveira, Luiz Pereira Ramos*,
Maria Aparecida Ferreira César-Oliveira

Departamento de Química, Centro de Pesquisa em Química Aplicada – CEPESQ,
Universidade Federal do Paraná – UFPR, CP 19081, 81531-990, Curitiba, PR, Brazil

*e-mail: luiz.ramos@ufpr.br

**see more at: SOLDI, R.A., *et al. Applied Catalysis. A, General* 2009, 361, 42.

Because homogeneous catalysis in alkaline medium is fast, simple and efficient, it still prevails as the best technological route for biodiesel manufacture¹⁻³. However, acid catalysis does have several important advantages: it is not affected by the presence of free fatty acids from the raw material, it does not produce soap, and it catalyzes esterification and transesterification reactions simultaneously. Therefore, acid catalysis should allow for straightforward biodiesel production from raw materials (oils and fat) with high acid numbers.

Heterogeneous catalysis has attracted a lot of interest from both the scientific and industrial areas. Various examples of esterification and transesterification reactions employing polymeric catalysts have been described in the literature^{4,5}. Functionalized reticulated polymers are generally used, mainly those containing sulfonated macroreticular and gelular polystyrene-divinylbenzene resins (PS-DVB-SO₃H)^{6,7}.

Compared with homogeneous catalysts, the heterogeneous counterparts offer well-known advantages such as easy product separation, facile catalyst recovery and reuse, and possibility of obtaining highly pure products. Furthermore,

heterogeneous catalysts are noncorrosive, thus dismissing the need for product washing, which leads to fewer residues. However, reagent and product diffusion to and from the resin is crucial for catalysis efficiency^{6,7}.

In this work, ion-exchange resins containing covalently bound sulfonic groups (SPS) have been developed and evaluated as acid heterogeneous catalysts for the simultaneous esterification and transesterification of vegetable oils and animal fat (Figure 1). The performance of these novel catalysts in the alcoholysis of beef tallow and refined soybean oil was investigated. For comparison purposes, the same reaction conditions were also used with the commercially available Amberlyst 15, a PS-DVB-SO₃H macroreticulated resin.

Introduction of sulfonic groups into the PS polymer increases the solid's hydrophilicity. In fact, large catalyst swelling is observed in polar medium, with no solubilization or morphological alterations to the SPS. This behavior is due to the formation of sulfone in the SPS cross-linkages. Many literature works^{8,9} report that depending on the sulfonation reaction conditions cross-link formation occurs via an intermolecular

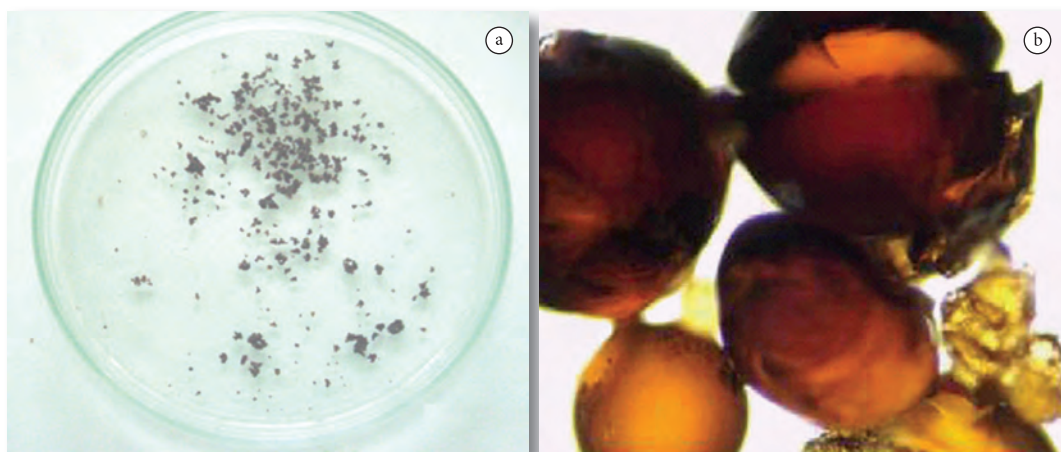


Figure 1. Images of ion-exchange resins containing covalently bound sulfonic groups, generated with (a) no magnification and with (b) optical microscopy (100x).

mechanism involving reaction between sulfonic groups belonging to different SPS chains.

Our results revealed an increase in the sulfonation degree of polystyrene (PS) with increasing fuming sulfuric acid/PS ratio. In the same way, high sulfonation degrees are obtained at longer reaction times. Indeed, allowing the reaction to proceed for 18 hours did not promote any significant increase (approximately 10%) in the amount of $-\text{SO}_3\text{H}$ groups present in SPS#218 compared with the sulfonation degree of compound SPS#23, obtained at 3 hours of reaction.

The thermal stability of the products containing a larger amount of sulfonic groups, which are thus considered more potential catalysts, was evaluated by thermogravimetric analysis (TGA). Figure 2 depicts the curves obtained for the linear PS sample as well as its sulfonation products SPS#23 and SPS#218. The curve corresponding to the macroporous resin Amberlyst 15 is also presented for comparison.

The TGA curve corresponding to PS (Figure 2) reveals there is no mass loss below 130 °C, while there is a relatively small mass loss between 130 and 300 °C (less than 3%). Random cleavages of the polymer chain take place at temperatures below 300 °C, but no volatile products are formed, leading to chains of low molar mass that are stable in this temperature range¹⁰. PS undergoes one-stage degradation; it is stable up to approximately 300 °C, but fast decomposition takes place thereafter. The onset of maximum degradation rate is around 390 °C, when 65% of the polymer has been degraded. No residues are observed above 440 °C^{11,12}.

The TGA curves of the SPS catalysts show that higher sulfonation degrees confer higher thermal stability to polystyrene. The catalysts SPS#23 and

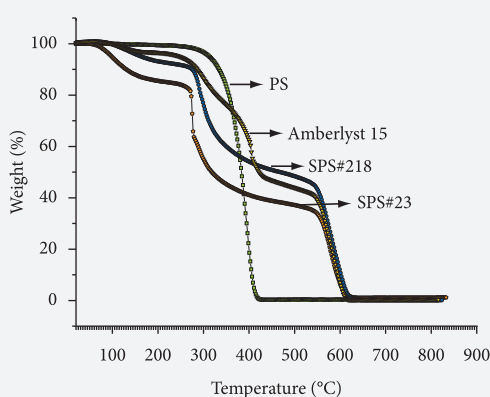


Figure 2. TGA curves of PS and polymeric catalysts.

SPS#218 have the same mass loss profile, involving three distinct temperature ranges (Figure 2). Because these catalysts are very hygroscopic, the first mass loss, between 50 and 130 °C, is probably due to dehydration. This loss corresponds to 11% and 2.5% of the initial masses of SPS#23 and SPS#218, respectively^{11,12}.

The second mass loss observed for the sulfonated materials SPS#23 and SPS#218 occurs between 200 and 400 °C, which is attributed to thermal desulfonation of the polymeric matrix with loss of SO_2 . More specifically, this second event takes place between 260 and 410 °C and corresponds to 43% and 39% of the initial mass of SPS#23 and SPS#218, respectively. The maximum degradation rate for this thermal decomposition stage is observed at 275 and 295 °C for SPS#23 and SPS#218, respectively. Slow decomposition followed by a third mass loss is detected between 530 and 630 °C. Mass losses of 36% and 47% are obtained for SPS#23 and SPS#218, respectively, assigned to polymeric matrix degradation. In this stage, the maximum decomposition rate is seen around 580 °C, and no residues are observed above 640 °C^{11,12}.

Figure 2 also shows the TGA curve of the resin Amberlyst 15, with four distinct mass loss events. The loss between 50 and 200 °C is mainly due to water loss, corresponding to 4% of the total mass. The second stage, between 200 and 300 °C, is assigned to desulfonation of the reticulated resin, which starts above 200 °C and is maximal at 300 °C. The onset of cross-link cleavage occurs in parallel with SO_2 loss from desulfonation, between 320 and 400 °C. The fourth mass loss stage takes place above 400 °C, with maximum loss at 580 °C. This is ascribed to total support degradation, with loss of various aromatic compounds such as styrene, methyl-styrene, and benzene^{11,12}.

Because alcoholysis happens at temperatures well below the one where SPS degradation takes place (240 °C), the thermal behavior of the investigated catalysts indicate that they can be applied in these transesterification processes. In other words, there is no risk of polymeric matrix degradation and/or loss of catalytic activity throughout alcoholysis. Furthermore, the SPS obtained here have thermal behavior comparable to that of reticulated resins, demonstrating their large potential for catalysis.

The preliminary studies carried out with the SPS in amounts lower than 20 mol% did not give

any significant conversion into soybean oil methyl esters, even when reactions were performed for over 18 hours.

To improve product yield and understand the behavior of these novel SPS catalysts in soybean oil transesterification, we carried out a preliminary study by keeping the catalyst amount at a fixed value of 20 mol% and varying the reaction time, temperature, and methanol/oil molar ratio. In this way, soybean oil methyl esters were achieved by transesterification using SPS catalysts. There was no phase separation between the methyl esters and the glycerin phases in any of the experiments.

Characterization of the methyl esters and product purity evaluation were carried out by ^1H NMR. The typical double-double doublet of triacylglycerides was absent in the spectrum of the methyl esters, and a singlet in $\delta = 3.65$ ppm due to methoxyl groups was detected.

When the transesterification reaction was carried out near room temperature ($30\text{ }^\circ\text{C}$), conversions were very low, independently of the methanol/oil molar ratio. As for the reaction performed at $60\text{ }^\circ\text{C}$, excess alcohol was the most important variable. The maximum product yield (40%) obtained for lower methanol/oil molar ratios was achieved at 18 hours, whereas this same yield was reached within 6 hours at an alcohol/oil molar ratio of 100:1. Using the latter ratio yields as high as 85% were obtained at 18 hours. When the reaction was accomplished under intense boiling (Figure 3), the system was supplied with an amount of energy that seemed to dismiss the need for excess alcohol. This was evident from the fact that the curve profile obtained for catalyst performance at a methanol/oil molar ratio of 9:1 was similar to that of the reaction carried out with a methanol/oil molar ratio of 100:1, leading to yields higher than 70% at 18 hours. The best results were obtained with the ratio 100:1, which led to yields higher than 90% at 18 hours of reaction (Figure 3).

Results from the conversion of soybean oil into its respective methyl esters demonstrated that product yield is strongly influenced by reaction time and temperature. In other words, higher temperatures and longer reaction times favor ester formation, a typical behavior of homogeneous catalysts¹³.

Although no linear relationship was clearly observed, higher alcohol/oil molar ratios also resulted in better product yields, independent of the

reaction time. This is related to the high sulfonation degree of the employed catalysts, because the sulfonic groups strongly interact with the alcohol and reduce the effective alcohol/oil molar ratio¹³. This limits the catalytic activity of SPS to the sulfonic groups present on its surface. Therefore, at higher alcohol/oil molar ratios the amount of alcohol is sufficient to promote catalyst swelling, enabling substrate access to the catalytic site and furnishing better product yields.

The data reveal that increased product yields are obtained in shorter reaction times if excess methanol is employed. Nevertheless, this condition does not pose any economic difficulties to the process because excess alcohol can be reused within the system.

On the basis of SPS performance in methanol and knowing that ester formation depends on temperature and alcohol/oil molar ratio, we decided to substitute methanol for ethanol and maintain the conditions in which the catalyst led to better conversion. We also evaluated SPS behavior in alcohol with different water percentages, once this variable influences product yield negatively¹⁻³.

Our results have shown that high ethyl ester yields are little influenced by the ethanol water percent. Anhydrous ethanol and absolute ethanol lead to the same oil conversion. The use of methanol as a transesterification agent for soybean oil results in methyl ester yields comparable to those of ethyl esters.

It is known that acidity impairs the use of base catalysis in homogeneous medium because of preferential soap formation¹⁻³. For this reason, the performance of the SPS catalysts in the conversion of raw materials with high acidity levels and low added value was also investigated.

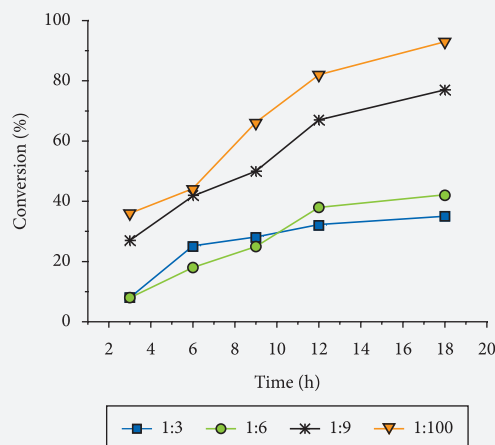


Figure 3. Soybean oil transesterification at $90\text{ }^\circ\text{C}$ under different methanol/oil molar ratios.

Beef tallow samples with acidity levels of 53 mg KOH/g were also assayed and the SPS catalyst was very efficient for (trans)esterification, being the yields comparable to those obtained with refined soybean oil in the same conditions.

No phase separation was observed between the ethyl ester and glycerin phases after SPS and ethanol removal, in all the experiments. Once the ¹H NMR analysis showed high conversion as well as the absence of glycerin in the ethyl esters, these results suggest that the developed catalyst plays two roles: besides catalyzing transesterification, it promotes ester purification, dismissing the need for product washing with water.

No ethyl ester formation occurred when the commercially available resin Amberlyst 15 was employed in the same experimental conditions. When methanol was used for transesterification, the resin led to 13% conversion only. These facts demonstrate that the good results obtained with the SPS catalysts cannot be achieved with commercially available compounds that are already well-established acid catalysts for chemical and industrial processes. These results thus reinforce the enormous potential of the acid catalysts developed in this work.

The catalyst developed in this work has a number of advantages over commercial ion

exchange resins: it has a higher degree of active sites it remains insoluble in the reaction medium employed in the production of soybean methyl biodiesel, and it is more efficient than other heterogeneous acid catalysts reported in the literature, under our experimental conditions. Despite being apparently high compared with the excess alcohol employed in homogeneous base catalysis, the alcohol/oil molar ratio of 100:1 employed here is much lower than those reported in the literature for commercially available heterogeneous acid catalysts.

Our heterogeneous catalyst was also very efficient for the transesterification of refined soybean oil and beef tallow with ethanol, leading to high conversion even when the raw material has high acidity levels. Ethanolysis carried out at an ethanol/oil molar ratio of 100:1 leads to 85% and 75% ethyl esters in the case of soybean oil and beef tallow, respectively. The SPS catalysts were little influenced by the ethanol water percent.

In conclusion, sulfonated polymeric compounds obtained from linear polystyrene were shown to be efficient catalysts for the alcoholysis of refined vegetable oils, as well as lipid sources containing high acid numbers such as beef tallow and used cooking oil.

REFERENCES

1. FUKUDA, H., KONDO, A., NODA, H., 2001. Biodiesel fuel production by transesterification of oils. *J. Biosci. Bioeng.* 92, 405-416.
2. VICENTE, G., MARTÍNEZ, M., 2004. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *J. Aracil, Bioresour. Technol.* 92, 297-305.
3. MEHER, L.C., VIDYA D., NAIK, S.N., 2006. Technical aspects of biodiesel production by transesterification- a review. *Renew. Sust. Energ. Rev.* 10, 248-268.
4. OZBAY, N., OKTAR, N., TAPAN, N.A., 2008. Esterification of free fatty acids in Waste Cooking. Oils: Role of ion exchange resins. *Fuel* 87, 1789-1798.
5. MO, X., LOTERO, E., LU, C., LIU, Y., GOODWIN, J.G., 2008. A novel sulfated Carbon Composite solid acid catalyst for biodiesel synthesis. *Catal Lett.* 123, 1-6.
6. HOLUB, L., JERABEK, K., MOL, J., 2005. Influence of Partial Neutralization on Catalytic Activity of Ion Exchange. *Catal. A-Chem.* 231, 24-26.
7. LÓPEZ, D.E., GOODWIN JR, J.G., BRUCE, D.A., 2007. Transesterification of triacetin with methanol on Nafion[®] acid resins, *J. Catal.* 245, 381-391.
8. F. Kucera, J. Jancar, *Polym. Eng. Sci.* 38 (1998) 1-12.
9. MARTINS, C.R., RUGGERI, G., DE PAOLI, M.A., 2003. Synthesis in Pilot Plant Scale and Physical Properties of Sulfonated Polystyrene. *J. Brazil. Chem. Soc.* 14, 797-802.
10. MARTHEW, A.P., PACKIRISAMY, S., THOMAS, S., 2001. Studies on the thermal stability of natural rubber/polystyrene interpenetrating polymer networks: thermogravimetric analysis. *Polym. Degrad. Stabil.* 72, 423-439.
11. B.N. Jang, C.A. Wilkie, *Polymer.* 46 (2005) 293-2942.
12. COUTINHO, FERNANDA M. B., DELPECH, MARCIA C. E ALVES, LAIRTON S. Síntese e caracterização de poliuretanos aniônicos em dispersão aquosa à base de polibutadieno líquido hidroxilado, poli(glicol propilênico) e diisocianato de isoforona. *Polímeros*, 2000, vol.10, no.1, p.49-55. ISSN 0104-1428. A.S. Gomes, L. da Cunha, F.M. Coutinho, *Polímeros.* 14 (2004) 31-37.
13. REZENDE, S.M., SOARES, B.G., COUTINHO, F.M.B., REIS, S.C.M., REID, M.G., LACTHER, E.R., NASCIMENTO, R.S.V., 2005. Resinas sulfônicas como catalisadores. *Polímeros.* 15, 186-192.

BEEF TALLOW BIODIESEL PRODUCED IN A PILOT SCALE**

Michele Espinosa da Cunha¹, Laiza Canielas Krause¹, Maria Silvana Aranda Moraes¹,
Candice Schmitt Faccini¹, Rosângela Assis Jacques², Suelen Rodrigues Almeida¹,
Maria Regina Alves Rodrigues², Elina Bastos Caramão^{1*}

¹Chemistry Institute/Federal University of Rio Grande do Sul/UFRGS – Av. Bento Gonçalves, 9500, 91501-970, Porto Alegre, RS, Brazil

²Department of Organic Chemistry (DQO), Chemistry Institute (IQ), Federal University of Pelotas (UFPEL), Campus Universitário, s/nº – Caixa Postal 354, 96010-900, Pelotas/RS, Brazil

³Federal University of Pelotas/Federal University of Pampa (UFPEL/UNIPAMPA-Bagé), Brazil

*e-mail: elina@ufrgs.br

**see more at: DA CUNHA, M.E., *et al. Fuel Processing Technology* 2009, 90, 570.

The development of alternative fuels from renewable resources, like biomass, has received considerable attention in all countries, mainly in Brazil due to its high biodiversity. Biodiesel can be defined as fatty acid alkyl esters from vegetable oils or animal fats, for using as fuel in diesel engines and heating systems¹. In this context, the use of beef tallow for biodiesel production in the South of Brazil (Rio Grande do Sul) has gained special interest, since it allows the use of rejected materials from cattle slaughterhouses. Methyl esters are the product of transesterification of fat and oils with methanol using an alkaline catalyst (KOH). In addition, the process yields glycerol, which has large applications in the pharmaceutical, food and plastics industries¹⁻⁵. The process of transesterification is affected by the mode of reaction condition, alcohol/oil molar ratio, kind of alcohol, type and amount of catalysts, reaction time, temperature and purity of reactants⁵⁻¹⁰.

Diesel fuel plays an important role in the Brazilian economy and its development, since the majority of freight is based on the use of trucks. The diesel demand is continually increasing, requiring an alternative fuel that will be technically viable, economically competitive and ecologically correct¹⁻⁵. Biodiesel is an attractive alternative of diesel fuel because it is produced from renewable resources and involves lower emissions than petroleum diesel^{1,3}.

According the Brazilian Legislation, biodiesel is a biofuel derived from renewable biomass for use in cycle diesel motors or, under specific regulation, in the generation of another type of energy that can substitute partially or totally fossil fuel. biodiesel is

registered in EPA (USA Environmental Protection Agency) as fuel or as additive for fossil fuel. It can be used pure (100% - B100), in mixture with petroleum diesel (BX, with X > 5%), or in the range of 1 to 5%, as additive².

The use of biodiesel can promote a reasonable reduction in the main pollutant emissions like particulate material, total hydrocarbons and carbon monoxide, but it can increase nitrogen oxides (NOx)^{5,6,11-15}.

Besides these advantages, if the raw material of biodiesel was a reject of any other industrial or agricultural activity, an important environmental aspect is added. Beef tallow is one residual material from slaughterhouses which main destination is the soap industry, but when this market is overloaded, the fats are usually incinerated or disposed in a sanitary landfill. In both cases there is a pollutant impact. Thus the integrated use of industrial residues generated in slaughterhouses can avoid such problems, allowing new alternative job and minimizing the environmental impact of the accumulation of these residues⁴.

The objective of the present work is the optimization of the semi-industrial transesterification process of animal fats with methanol in the presence of KOH as catalyst. The produced biodiesel was evaluated according to the Brazilian official specification tests and it showed high quality.

The beef tallow used in the biodiesel production was acquired in some slaughterhouses in the area of Pelotas city, state of Rio Grande do Sul, Brazil. Its main characteristics were: iodine value in the range of 41.1 to 41.9 (g I₂/100 g) and the acid number, from 1.2 to 1.8 mg KOH/g.

The methanol and the potassium hydroxide, used in the transesterification process, were of commercial grade and acquired in the local market. The biodiesel used was produced by alkaline transesterification in a Biodiesel Pilot Plant located in the South of Brazil (installed in Federal University of Pelotas – UFPel).

Biodiesel was produced in a pilot plant (Figure 1) with the capacity of approximately 800 kg/day. The main reactor operated at ambient pressure and at fixed temperature which was maintained by electrical resistances. For the transesterification reaction about 800 kg of beef tallow (previously melted) were transferred to the main reactor, heated at 65 °C while 1.5% of KOH (wt/wt) related to the fat weight, was dissolved in methanol with a molar ratio of 6:1 (methanol to fat or oil) in an auxiliary reactor, and the mixture was added to the main reactor.

The reactants were stirred for 180 min at 400 rpm and then the stirrer was turned off and the reaction mixture was left in rest for 240 minutes to promoting the decantation by gravity of glycerol and methyl esters. After this time, the glycerol phase was discharged and methyl ester phase was washed with 180 L of hot acidified water (500 mL of commercial phosphoric acid) by stirring during 60 minutes to removing residual catalyst, glycerol, methanol and soaps. After the

separation of water phase, biodiesel is heated to 90 °C for 30 min to eliminate water and methanol residual, filtered (limit of 4 µm) and sent to storage tank.

Table 1 presents qualitative and quantitative composition of the fatty acids methyl esters of beef tallow and of the produced biodiesel. Table 2 shows the mass balance of the process of transesterification of beef tallow and some of the main properties of the produced biodiesel. This Table summarizes the results of 5 (five) experiments and, in the last column, it is showing the average values, only for illustrative purposes.

For the other analyses it was chosen the biodiesel produced in the experiment 2 (according Table 2) and the results are presented in Table 3. This Table also shows the properties of a blend B2 (2 % of biodiesel in diesel) and of a diesel used as reference.

From the data presented previously it is possible to conclude that the alkaline transesterification of beef tallow with methanol produces a biodiesel with high quality and also with a good conversion ratio. The process is possible but the economical viability must be improved by recovering methanol and glycerol.

Moreover, in a previous work¹⁶ it was shown that other blends biodiesel/diesel, with higher levels of beef tallow biodiesel (B5, B10, B20 and B30) have similar or better fuel properties than diesel,

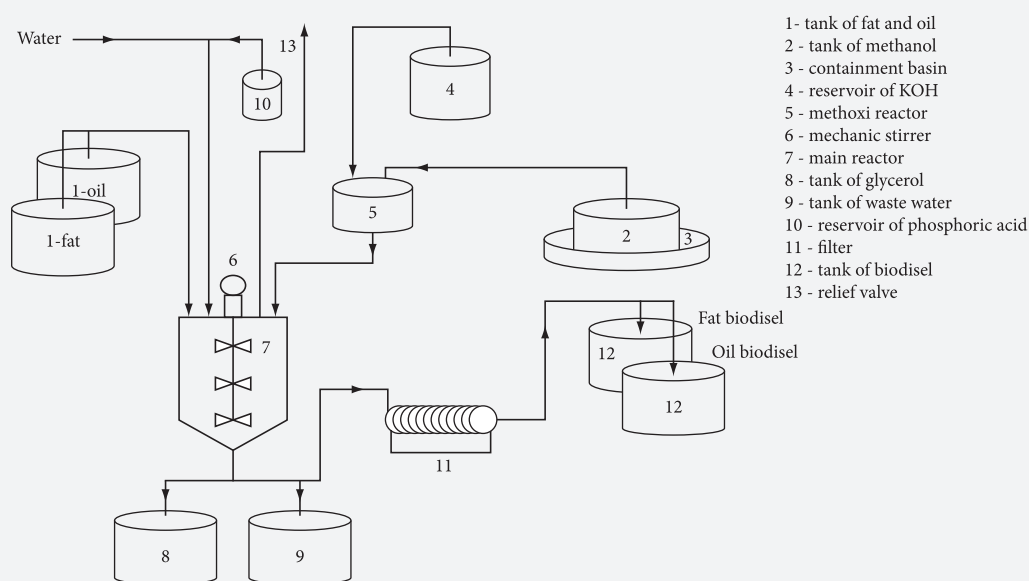


Figure 1. Flow sheet of the transesterification process.

indicating that this is a good way to improve certain properties of diesel without loss of efficiency or increase in consumption. This project is a first step for the construction of a big plant (120,000 kg/day) of production of biodiesel from beef tallow in Rio Grande do Sul, south of Brazil. This plant will use alkaline catalyst and also will work with other

kinds of oils, mainly from animal origin. For this purpose, these results demonstrated that this objective can be achieved with little modifications, mainly with the addition of two steps: (1) a recovery of methanol from glycerin and from biodiesel and (2) an improvement in the separation of biodiesel by using a centrifuge.

Table 1. Qualitative and quantitative composition of the fatty acids methyl esters in beef tallow and in the produced biodiesel.

designation	acid name	% composition	mw _{acid}	mw _{ester}
C14:0	Miristic	2.72	228	242
C15:0	Pentadecanoic	0.86	242	256
C16:1	Palmitoleic	2.02	254	268
C16:0	Palmitic	25.33	256	270
C17:0	Heptadecanoic	1.67	270	284
C18:2	Linoleic	0.75	280	294
C18:1 (<i>cis</i>)	Oleic	29.87	282	296
C18:1 (<i>trans</i>)	Elaidic	1.82	282	296
C18:0	Stearic	34.70	284	298
C20:0	Arachidic	0.28	312	326
mass ratio of saturated and unsaturated		1.90		
average molecular weight (amw)		273,5 ^(a)	858.5 ^(b)	287.6 ^(c)

(a) amw of acids in the beef tallow = $\sum (\% \text{ composition} \times \text{mw}_{\text{acid}})$
 (b) amw of beef tallow (g/mol) = $3 (\text{amw}_{\text{acid}}) + \text{mw}_{\text{glycerol}} - 3 (\text{mw}_{\text{water}})$
 (c) amw of biodiesel (g/mol) = $\sum (\% \text{ composition} \times \text{mw}_{\text{ester}})$

Table 2. Mass balance of the process of transesterification of beef tallow and main properties of the produced biodiesel.

		Experiments					
		1	2	3	4	5	average
amount of reagents and products (kg)	beef tallow (mw = 858.5 g/mol)	743	551	565	679	696	647
	methanol (mw = 32 g/mol)	141	139	131	171	176	152
	biodiesel (mw = 287.6 g/mol)	685	570	568	650	720	639
	glycerol (mw = 92 g/mol)	136	98	92	115	110	110
number of mols of reagents and products	beef tallow	865	642	658	791	811	753
	methanol	4406	4344	4094	5344	5500	4738
	biodiesel	2382	1982	1975	2260	2503	2220
	glycerol	1478	1065	1000	1250	1196	1198
molar excess of methanol (*)		2595	1925	1974	2372	2431	2259
biodiesel properties	mass conversion (%)	92.2	103	100.5	95.7	103	99.04
	molar conversion (%)	91.8	103	100.1	95.3	103	98.64
	IA (mg KOH/g)	0.8	0.3	0.8	0.6	0.7	0.64
	Esters (%)	97	97	95	96	97	96.4
	MeOH (%)	0.3	0.1	0.2	0.1	0.1	0.16
	II (g I ₂ /100 g)	41.8	41.5	41.2	41.7	41.8	41.6

Table 3. Some fuel properties of beef tallow biodiesel, compared with diesel

Properties	Limits* (D e B2)	B100(#)	B2(##)	Diesel
Density (20°C kg L ⁻¹)	0.820 a 0.865	0.872	0.844	0.844
Flash point (min., °C)	min. 38.0	156.7	43.0	40.7
Kinematic viscosity (40°C, mm ² s ⁻¹)	2.0 a 5.0	5.3	2.7	2.7
CFPP (max. °C)	appoint	14.3	-11.7	-15.3
Distillation range (°C)				
Initial temperature (°C)	–	307.1	135.7	137.6
10 %		325.7	176.0	172.1
50%	–	331.0	270.7	267.0
90%	360 max	343.0	363.1	372.1
Final temperature (°C)	–	344.4	400.9	400.1
Cetane index	–	60.35	47.15	46.52
Na (mg kg ⁻¹)	10 max	1.63	–	–
K (mg kg ⁻¹)	10 max	< 0.50	–	–
Esters	appoint	97	–	–
Methanol	0.5% max	0.1	–	–
Soaps** (ppm)	appoint	76.06	–	–

(*) Brazilian specification to Diesel (D) and B2 (blend with 2 % of biodiesel in diesel)

(**) AOCs method Cc 17-79, soap in oil

(#) pure beef tallow biodiesel (100 %)

(##) blend of beef tallow biodiesel and petrochemical diesel (2 %)

REFERENCES

1. Srivastava, A., Prasad, R., 2000. Triglycerides-based diesel fuels, *Renewable and Sustainable Energy Reviews* 4, 111–133.
2. Ferrari, R.A., Oliveira, V.S., Scabio, A., 2005. Biodiesel de soja – Taxa de conversão em ésteres etílicos, caracterização físico-química e consumo em gerador de energia, *Quimica Nova* 28, 19–23.
3. Leung, D.Y.C., Koo, B.C.P., Guo, Y., 2006. Degradation of biodiesel under different storage conditions, *Bioresource Technology* 97, 250–256.
4. Neto, P.R.C., Rossi, L.F.S., Zagonel, G.F., Ramos, L.P., 2000. Produção de biocombustível alternativo ao óleo diesel através da transesterificação de óleo de soja usado em frituras, *Quimica Nova* 23, 531–537.
5. Meher, L.C., Sagar, D.V., Naik, S.N., 2006. Technical aspects of biodiesel production by transesterification – a review, *Renewable and Sustainable Energy Reviews* 10, 248–268.
6. Sheehan, J., Camobreco, V., Duffield, J., Graboski, M., Shapouri, H., 1998. An Overview of Biodiesel and Petroleum Diesel Life Cycles, U.S. Department of Energy, Office of Scientific and Technical Information, in <http://www.biodiesel.com/PDF/Biodiesel%20Life%20Cycle.pdf>, accessed in April, 30, 2008.
7. Ma, F. Clements, D.L. Hanna, A.M., 1998. Biodiesel fuel from animal fat. Ancillary studies on transesterification of beef tallow, *Industrial Engineering Chemical Research* 37, 3768–3771.
8. Freedman, B., Pryde, E.H., Mounts, T.L., 1984. Variables affecting the yields of fat esters from transesterified vegetable oils, *Journal of American Oil Chemist Society* 61, 1638–1643.
9. Van Gerpen, J., 2005. Biodiesel processing and production, *Fuel Processing and Technology* 86, 1097–1107.
10. Marchetti, J.M., Miguel, V.U., Errazu, A.F., 2007. Possible methods for biodiesel production, *Renewable and Sustainable Energy Reviews* 11, 1300–1311.
11. Çetinkaya, M., Ulusoy, Y., Tekin, Y.L., Karaosmanoglu, F., 2005. Engine and winter road test performances of used cooking oil originated biodiesel, *Energy Conversion Management* 46, 1279–1291.
12. Fernando, S., Hall, C., Jha, S., 2007. NOx reduction from biodiesel fuels, *Energy & Fuels* 21, 376–382.
13. Lebedevas, S., Vaicekaskas, A., Lebedeva, G., Makareviciene, V., Janulis, P., Kazancev, K., 2006. Use of waste fats of animal and vegetable origin for the production of biodiesel fuel: quality, motor properties, and emissions of harmful components, *Energy & Fuels* 20, 2274–2280.

14. Kumar, M.S., Kerihuel, A., Bellettre, J., Tazerout, M., 2005. Experimental investigations on the use of preheated animal fat as fuel in a compression ignition engine, *Renewable Energy* 30, 1443–1456.
15. Canakci, M., 2007. Combustion characteristics of a turbocharged DI compression ignition engine fueled with petroleum diesel fuels and biodiesel, *Bioresource. Technology* 98, 1167–1175.
16. Moraes, M.S.A., Krause, L.C., da Cunha, M.E., Faccini, C.S., de Menezes, E.W., Veses, R.C., Rodrigues, M.R.A., Caramão, E.B., 2008. Tallow biodiesel: properties evaluation and consumption tests in diesel engine, *Energy & Fuels* 22, 1949–1954.



Overview of the pilot plant



Details of the transesterification reactor



Details of the methoxide reactor



First biodiesel production



Mixtures diesel / biodiesel (beef tallow)



Fuel supply with the produced biodiesel, carried out on the Pilot Plant
 Note: one truck was fueled with B40 blends during one year (2008), including summer and winter in Rio Grande do Sul.

SIMULTANEOUS DETERMINATION OF Cd AND Fe IN BEANS AND SOIL OF DIFFERENT REGIONS OF BRAZIL USING HIGH-RESOLUTION CONTINUUM SOURCE GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY AND DIRECT SOLID SAMPLING**

Lisia M.G. dos Santos^{1,2}, Bernhard Welz^{1,3*}, Rennan G.O. Araujo¹, Silvana do C. Jacob², Maria Goreti R. Vale^{3,4}, Andreas Martens⁵, Irland B. Gonzaga⁶, Helmut Becker-Ross⁷

¹Departamento de Química, Universidade Federal de Santa Catarina – UFSC, Florianópolis, SC, Brazil

²Instituto Nacional de Controle de Qualidade em Saúde – Fiocruz, Rio de Janeiro, RJ, Brazil

³Instituto Nacional de Ciência e Tecnologia – INCT de Energia e Ambiente, Universidade Federal da Bahia – UFBA, Salvador, BA, Brazil

⁴Instituto de Química, Universidade Federal do Rio Grande do Sul – UFRGS, Porto Alegre, RS, Brazil

⁵Institute for Inorganic and Analytical Chemistry, Technical University Braunschweig, Germany

⁶Departamento de Alimentos e Nutrição Experimental, Universidade de São Paulo – USP, São Paulo, SP, Brazil

⁷ISAS – Institute for Analytical Sciences, Department of Interface Spectroscopy, Berlin, Germany

*e-mail: welz@qmc.ufsc.br

**see more at: DOS SANTOS, L.M.G., *et al. Journal of Agricultural and Food Chemistry* 2009, 57, 10089.

Since soil contamination by anthropogenic sources has increased significantly in many parts of the world, it has become an important environmental issue in industrialized countries. Heavy metals might influence the soil quality, the agricultural production and the groundwater quality, affecting human health through the water supply and foods¹. The content of metallic elements in foods depends on their concentration in the soil, their availability, and their capacity to be incorporated by the plants.

Cadmium is extremely toxic even at low concentration; it was classified as carcinogenic of group 1 by the International Agency for Research on Cancer (IARC)², and set in the 7th position in the list of the substances most aggressive to health and to the environment by the Program for Answers Reparations and Environmental Responsibilities (Cercla) of the ATSDR-EPA³. Concern has therefore been expressed in several recent publications about pollution in environmental and health areas, because humans and animals are constantly exposed to such risks through air, soil, water and food⁴.

Iron, in contrast, is an essential element, and in developing countries, iron deficiency

(anemia) affects predominantly the low-income group of the population, and it has in general a great impact on the quality of life in so-called Third World Countries. The increased risk for various infectious diseases is directly related to the reduction of immune resistance generated by anemia⁵. Legumes, such as beans, constitute the main source of proteins and are a good source of mineral elements, such as iron, for large groups of population in Latin America and Africa. However, soil contamination affects the iron absorption and could cause damage to public health⁶.

Recently a method for the simultaneous determination of cadmium and iron in grain products has been developed by our group⁷ using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS)⁸ and direct solid sampling (SS) analysis. The latter technique is particularly suited for fast screening analyses, as essentially no sample preparation is necessary, avoiding in addition all potential sources of error associated with this stage of an analysis. Direct SS analysis also provides the highest possible sensitivity, as no dilution at all is involved in this technique. In addition, HR-CS GF AAS has been shown to be an extremely robust technique that

makes possible direct SS analysis of complex samples using aqueous standards for calibration⁹.

All experiments have been carried out using a high-resolution continuum source atomic absorption spectrometer, which consists of a high-intensity xenon short-arc lamp operating in a hot-spot mode, a high-resolution double monochromator and a CCD array detector⁸. The primary resonance line for Cd at 228.802 nm, and the adjacent secondary line for Fe at 228.726 nm have been used for the simultaneous determination of the two elements.

One of the requirements for that approach is that a compromised graphite furnace temperature program can be established that makes possible the simultaneous determination of the analytes of interest without too many sacrifices in sensitivity and overall performance. This condition could be fulfilled in the simultaneous determination of Cd and Fe in grain products using W-Ir as permanent chemical modifier and a two-step atomization⁷. Another requirement is that the sensitivity ratio between the elements to be determined at the available analytical lines corresponds roughly to the concentration ratio of the analytes in the samples to be analyzed. This condition was also fulfilled in the analysis of grain products⁷, as

the iron line 228.726 nm is about two orders of magnitude less sensitive than the primary line 248.327 nm, and about three orders of magnitude less sensitive than cadmium at the 228.802 nm line. This situation is shown in Figure 1 for the CRM Brown Bread, and it has been anticipated that the same could apply for the bean samples. However, it could also be expected that the developed method could not be transferred directly to soil samples, which are usually rich in iron, particularly in many regions of Brazil.

The proposed method has been used for the simultaneous determination of cadmium and iron in bean and soil samples from different regions of Brazil. Fourteen bean samples and nine soil samples, collected in nine states of Brazil, were investigated in this study. Most of the samples were collected at experimental farms of Embrapa or similar institutions. The soil samples were always taken close to the area where the beans were grown. The results of the investigation, using aqueous standards for calibration, are shown in Table 1.

The concentration of cadmium in most of the bean samples, except for two, was below $2 \mu\text{g kg}^{-1}$, a value that is well below the limits established by the Codex Alimentarius (0.2 mg kg^{-1}) and the

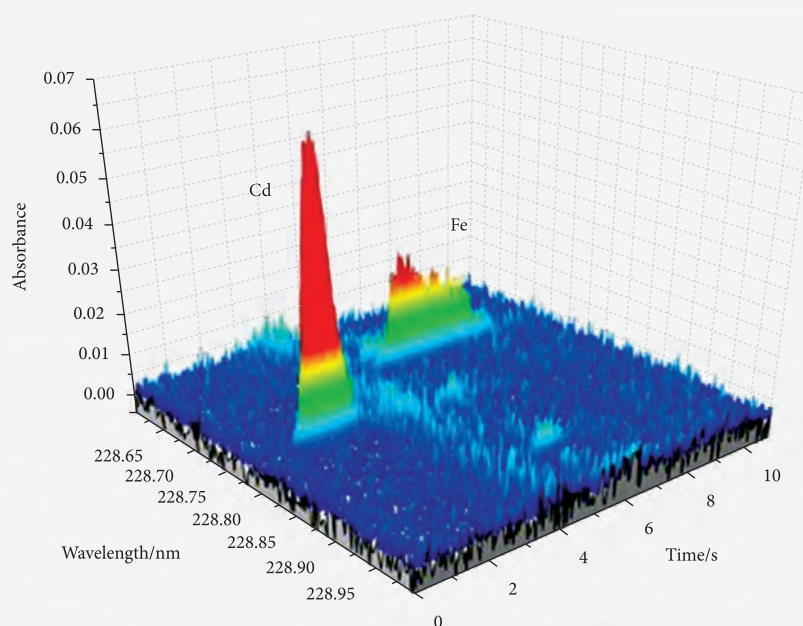


Figure 1. Time- and wavelength-resolved absorbance spectrum for the BCR CRM 191 (Brown Bread) in the vicinity of the cadmium resonance line at 228.802 nm; pyrolysis temperature: 700 °C; atomization temperature: 1700 °C for Cd and 2600 °C for Fe; W-Ir mixed permanent modifier.

Table 1. Results obtained for the determination of cadmium and iron in bean and soil samples using SS-HR-CS GF AAS and aqueous standards for calibration.

State	Beans		Soil		
	Type	Cd / $\mu\text{g kg}^{-1}$	Fe / mg kg^{-1}	Cd / $\mu\text{g kg}^{-1}$	Fe / g kg^{-1}
Amazonas	brown	10 ± 1	57 ± 10	315 ± 54	67 ± 22
	black	24 ± 6	80 ± 6		
Pará	brown	< 2	57 ± 6	< 14	4.7 ± 1.6
Ceará	brown	< 2	61 ± 6	30 ± 6	78 ± 16
Goiás	white	< 2	99 ± 16	57 ± 8	>200
Mato Grosso do Sul	brown	< 2	127 ± 28	24 ± 1	47 ± 10
Minas Gerais	brown	< 2	104 ± 13	< 14	133 ± 63
	brown	< 2	117 ± 19		
Paraná	black	< 2	103 ± 12	28 ± 1	87 ± 36
Santa Catarina	black	< 2	111 ± 21	62 ± 4	11 ± 2
	brown	< 2	69 ± 13	14 ± 5	< 0.5
Rio Grande do Sul	black	< 2	161 ± 21	40 ± 6	118 ± 44
	brown	< 2	159 ± 16		

Brazilian National Health Surveillance Agency–ANVISA (1.0 mg kg^{-1})¹⁰. It is interesting to note that the only cadmium concentrations above the LOQ have been found in beans that were grown on a soil the cadmium content of which was about an order of magnitude above the average of all the other soils. This suggests a direct correlation between the cadmium content in soil and in beans, although the number of samples analyzed here is clearly too small to allow any statistical comparison. The values obtained for cadmium in soil samples were between < 14 and $315 \mu\text{g kg}^{-1}$, with an average around $31 \mu\text{g kg}^{-1}$, not considering the soil from Amazonas. These values are well below the limits established (3.0 mg kg^{-1}) for agricultural soils in Europe.

The content of iron in beans ranged from 57 mg kg^{-1} to 159 mg kg^{-1} . According to Embrapa the amount of iron in beans should be approximately 76 mg kg^{-1} , which corresponds to 29% of women's daily needs and 55% of men's needs¹¹. Hence, we can say that the beans produced in Brazil do have a sufficiently high iron content, which is in contrast to many grain products, which do not

provide a sufficient iron supply⁷. The iron content in the investigated soils ranged from < 0.5 g kg^{-1} to 133 g kg^{-1} . The high concentration of iron, in the soil samples, has been according to expectation because of the reddish color of most of the samples, characteristic of the iron oxide. There has been no correlation between the iron content in the soil that varied by more than two orders of magnitude, and that in the beans grown on that soil, which varied by less than a factor of three. This means that the iron uptake by the plants is regulated by a mechanism that is independent of the iron content in the soil and that also assures a sufficient iron content in the beans in case the soil is low in iron.

Although only two bean samples had detectable cadmium content, the conclusion appears to be justified that there is a correlation between the cadmium content in the beans and in the soil. On the other hand there was no correlation at all between the iron content in the soil and in the beans. It has also not been possible to establish a link between the cadmium and the iron concentration in the soil, as has been proposed in the literature.

REFERENCES

1. BEACH, J., TUME, P., LONGAN, L., REVERT, F., BECH, J., TUME, L., TEMPIO, M., 2008. Concentration of Cd, Cu, Pb, Zn, Al, and Fe in soils of Manresa, NE Spain. *Environ. Monit. Assess.* 14, 257–266.
2. World Health Organization. Safety evaluation of certain food additives and contaminants. WHO food additives Series: 59. Geneva: IPCS-International Programme on Chemical Safety, 2008 <http://www.codexalimentarius.net>
3. Agency for Toxic Substances and Disease Registry. Top 20 Hazardous Substances from the CERCLA Priority List of Hazardous Substances for 2005. <http://www.atsdr.cdc.gov/>
4. MIRLEAN, N., ROISENBERG, A., 2006. The effect of emissions of fertilizer production on the environment contamination by cadmium and arsenic in southern Brazil. *Environ. Pollut.* 143, 335–340.
5. MOURA, N.C., CANNIATTI-BRAZACA, S.G., 2006. Avaliação da disponibilidade de ferro de feijão comum (*Phaseolus vulgaris* L.) em comparação com carne bovina. *Cienc. Tecnol. Aliment.* 26, 270–276.
6. LAPARRA, J.M., GLAHN, R.P., MILLER, D.D., 2008. Bioaccessibility of phenols in common beans (*Phaseolus vulgaris* L.) and iron (Fe) availability to Caco-2 cells. *J. Agric. Food Chem.* 56, 10999–11005.
7. DOS SANTOS, L.M.G., ARAUJO, R.G.O., WELZ, B., JACOB, S.C., VALE, M.G.R., 2009. Becker-Ross, H. Simultaneous determination of Cd and Fe in grain products using direct solid sampling and high-resolution continuum source electrothermal atomic absorption spectrometry. *Talanta* 78, 577-583.
8. WELZ, B., BECKER-ROSS, H., FLOREK, S., HEITMANN, U., 2005. High-Resolution Continuum Source AAS - The Better Way to do Atomic Absorption Spectrometry; Wiley-VCH: Weinheim, Germany, 2005.
9. WELZ, B., VALE, M.G.R., BORGES, D.L.G., HEITMANN, U., 2007. Progress in direct solid sampling analysis using line source and high-resolution continuum source electrothermal atomic absorption spectrometry. *Anal. Bioanal. Chem.* 389, 2085–2095.
10. BRASIL. Decreto nº 55871, de 26 de março do 1965. Modifica o Decreto nº 50040, de 24 de Janeiro de 1961, referente a normas reguladoras do emprego de aditivos para alimento, alterado pelo Decreto nº 691 de 13 de Abril de 1962. *Diário Oficial [da] República Federativa do Brasil, Poder Executivo, Brasília, DF, 09 abr. 1965.*
11. Empresa Brasileira de Pesquisa Agropecuária– Composição nutricional do Feijão. <http://www.cnpaf.embrapa.br/parperfeito/feijao/composicao.htm>

DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR DETERMINATION OF COBALT IN WATER SAMPLES**

Patrícia Xavier Baliza^{a,b}, Leonardo Sena Gomes Teixeira^a, Valfredo Azevedo Lemos^{b*}

^aInstituto de Química, Universidade Federal da Bahia – UFBA, Campus Universitário de Ondina, 40170-280 Salvador, BA, Brazil

^bNúcleo de Química Analítica da Bahia – NQA, Laboratório de Química Analítica – LQA, Universidade Estadual do Sudoeste da Bahia – UESB, Campus de Jequié, 45506-191 Jequié, BA, Brazil
*e-mail valfredoazevedo@yahoo.com.br

**see more at: BALIZA, P.X., et al. *Microchemical Journal* 2009, 93, 220.

The quantification of metal species in various matrices has been performed by different techniques, including spectrophotometry, atomic absorption spectrometry (AAS), and inductively coupled plasma optical emission spectrometry (ICP OES), among others. However, these techniques do not have adequate sensitivity and selectivity for some analysis. Thus, procedures of separation or preconcentration may be required before the spectrometric determination of trace elements^{1,2}.

Dispersive liquid-liquid microextraction (DLLME) is a preconcentration technique that employs a ternary system of solvents. This technique was reported for the first time in a procedure for the determination of organophosphorus pesticides in water³. However DLLME has also been used for extraction and preconcentration of inorganic compounds, offering advantages such as ease of operation, use of small quantities of sample and organic solvents, speed of analysis, low cost and high recoveries and enrichment factors^{4,5}.

In DLLME, a mixture containing appropriate amounts of extraction solvent and disperser solvent is injected rapidly into an aqueous sample with the aid of a syringe. Then, a cloudy solution is formed and the analyte is extracted into the interior of droplets of extraction solvent. After extraction, the phase separation is accomplished by centrifugation, and the analyte is determined in the sedimented phase. For the determination of metal trace elements, a complexing reagent should be dissolved in the mixture⁶.

In this work, a procedure for preconcentration of cobalt using dispersive liquid-liquid microextraction with the reagent Br-TAO as complexing reagent

was developed. After optimization of experimental variables and determination of analytical features, the procedure was applied to the determination of cobalt in water samples.

A solution containing cobalt was adjusted to pH with an appropriate buffer solution. Five milliliters of the cobalt solution were added to a test tube. Then, a solution containing 50.0 μ L of carbon tetrachloride, 2.0 mL of methanol, and 50.0 μ L of a Br-TAO solution was prepared. The methanolic solution was immediately injected in the solution of the metal using a 5.0 mL glass syringe. The resulting cloudy solution was centrifuged for 2.0 minutes at 5000 rpm. After centrifugation, a reddish residue was sedimented at the bottom of the tube. This residue was injected into the flame atomic absorption spectrometer (FAAS) using the system described in the following item.

Many procedures using DLLME for preconcentration of metals employ electrothermal atomic absorption spectrometry (ETAAS) as a technique of detection. In this case, the introduction of rich phase is simple, because the detection equipment requires a small and defined sample volume. When FAAS is used, special attention should be taken in the introduction of the rich phase, because the sample volume required for the direct reading in equipment is usually greater than that obtained when microextraction procedure is employed. In this work, a simple injection device was used in FAAS. The schematic representation of the strategy used for sample introduction is shown in Figure 1. The system consists of a six-port valve, a peristaltic pump, a plastic syringe and capillary tubes of Teflon. The rich phase is aspirated using a plastic syringe until the liquid fill the entire volume

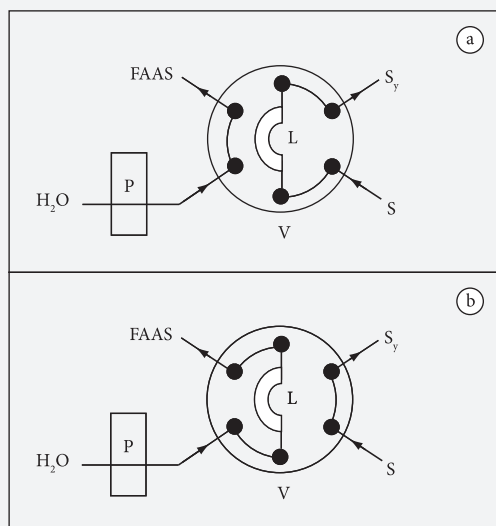


Figure 1. System for injection of rich phase in flame atomic absorption spectrometer (FAAS). V, six-port rotary valve; L, sample loop.

of the sample loop. Then, the position of the valve is changed and a stream of water carries the enriched phase into the FAAS and a transient signal is obtained. The volume of sample loop was set at $20 \mu\text{L}$.

The analytical characteristics of the proposed procedure were calculated under the optimized conditions. These characteristics were calculated using the values of the signals for analytical curve. The detection limit, calculated as $3s_b/b$, where s_b is the standard deviation of the blank and b is slope of the linear section of calibration graph, was $0.9 \mu\text{g L}^{-1}$. The limit of quantification ($10s_b/b$) was $3.0 \mu\text{g L}^{-1}$. The system shows linearity between 3.0 and $100.0 \mu\text{g L}^{-1}$. The calibration curve over this interval was determined to be $A = 3.90 \times 10^{-3} + 1.39 \times 10^{-4} C$, where A is the analytical signal, measured as absorbance, and C is the concentration of cobalt in the solution ($\mu\text{g L}^{-1}$).

The proposed method was applied to the determination of cobalt in real samples of water and certified reference material NIST 1570a, Spinach leaves. In order to determine the accuracy of the method, the reference material was digested and the liquid sample was submitted to preconcentration procedure. The content of cobalt obtained by the proposed procedure was $0.43 \pm 0.07 \mu\text{g g}^{-1}$, which agrees with the certified value $0.39 \pm 0.05 \mu\text{g g}^{-1}$. Cobalt was determined after application of the proposed procedure to samples of drinking water, river water and well water, collected in the city of Jequié, Bahia. The results for three individual determinations are shown in Table 3. Known amounts of metal were also added for the calculation of recovery for each sample. The values of recoveries ranged from 94 to 104%, demonstrating the applicability of the method.

In the proposed procedure, the reagent Br-TAO was successfully used as complexing for preconcentration of cobalt using dispersive liquid-liquid a microextraction. The method is simple, easy to use and economic. The low cost is related mainly to small amounts of solvents required. The small amounts of carbon tetrachloride and methanol also minimizes the toxicity of the method. Another interesting feature of the method is speed. After injection of the mixture Br-TAO/methanol/carbon tetrachloride, the solution was immediately cloudy. The rich phase is injected into the FAAS after rapid centrifugation. There is a need for low volume of sample, particularly desirable property when there is limitation in the sample amount. The advantages cited and the analytical characteristics obtained make the method a good alternative to the determination of cobalt in routine analysis.

REFERENCES

1. WEN, X., WU, P., XU, K., WANG, J., HOU, X., 2009. On-line precipitation-dissolution in knotted reactor for thermospray flame furnace AAS for determination of ultratrace cadmium. *Microchem. J.* 91, 193-196.
2. LEMOS, V.A., GAMA, E.M., LIMA, A.D., 2006. On-line preconcentration and determination of cadmium, cobalt and nickel in food samples by flame atomic absorption spectrometry using a new functionalized resin. *Microchim. Acta* 153, 179-186.
3. REZAEI, M., ASSADI, Y., HOSSEINI, M.M., AGHAEI, E., AHMADI, F., BERIJANI, S., 2006. Determination of organic compounds in water using dispersive liquid-liquid microextraction. *J. Chromatogr. A* 1116, 1-9.
4. FARAJZADEH, M.A., BAHRAM, M., MEHR, B.G., JONSSON, J.A.K., 2008. Optimization of dispersive liquid-liquid microextraction of copper (II) by atomic absorption spectrometry as its oxinate chelate: Application to determination of copper in different water samples. *Talanta* 75, 832-840.
5. BIDARI, A., JAHROMI, Z.E., YAGHOUB, A., HOSSEIN, M.R.M., 2007. Monitoring of selenium in water samples using dispersive liquid-liquid microextraction followed by iridium-modified tube graphite furnace atomic absorption spectrometry. *Microchem. Journal* 87, 6-12.
6. BALIZA, P.X., TEIXEIRA, L.S.G., LEMOS, V.A., 2009. A procedure for determination of cobalt in water samples after dispersive liquid-liquid microextraction. *Microchemical Journal* 93, 220-224.

MULTICOMPONENT COUPLING REACTIONS IN THE SYNTHESIS OF THIOSEMICARBAZONES**

Silvio Cunha^{1,2*} and Tiago Lima da Silva^{1,2}

¹Instituto de Química, Universidade Federal da Bahia, Campus de Ondina, Salvador - BA, 40170-290 Brazil

²INCT de Energia e Ambiente, UFBA, 40170-290 Salvador, BA, Brazil

*e-mail: silviodc@ufba.br

**see more at: CUNHA, S.D. and DA SILVA, T.L. *Tetrahedron Letters* 2009, 50, 2090.

Nowadays, chemists are faced with environmental concerns that demand new procedures and/or procedure improvements where atom economy, minimal waste production, and energy/cost-effective preparations should be prime considerations¹⁻³. In this scenario, multicomponent reactions represent an advanced approach to achieve efficient target and diversity-oriented synthesis⁴⁻⁷.

Thiosemicarbazones and their metal complexes derivatives are an essential structural unit with a wide range of biological and pharmacological properties, and are versatile building blocks in the synthesis of densely substituted heterocycles.³

However, the available synthetic methodologies for this class of compound are stop-and-go approaches involving isolation and purification of each prepared intermediate, which are time, solvent and energy consuming procedures⁸⁻¹².

The most successful routes to access thiosemicarbazones consist of step-by-step reactions of hydrazine with different electrophiles (Figure 1).

We initiated our study exploring the possibility of a multicomponent reaction towards thiosemicarbazones by mixing in the same pot one equiv of benzaldehyde, phenyl isothiocyanate and hydrazine in methanol under reflux, according

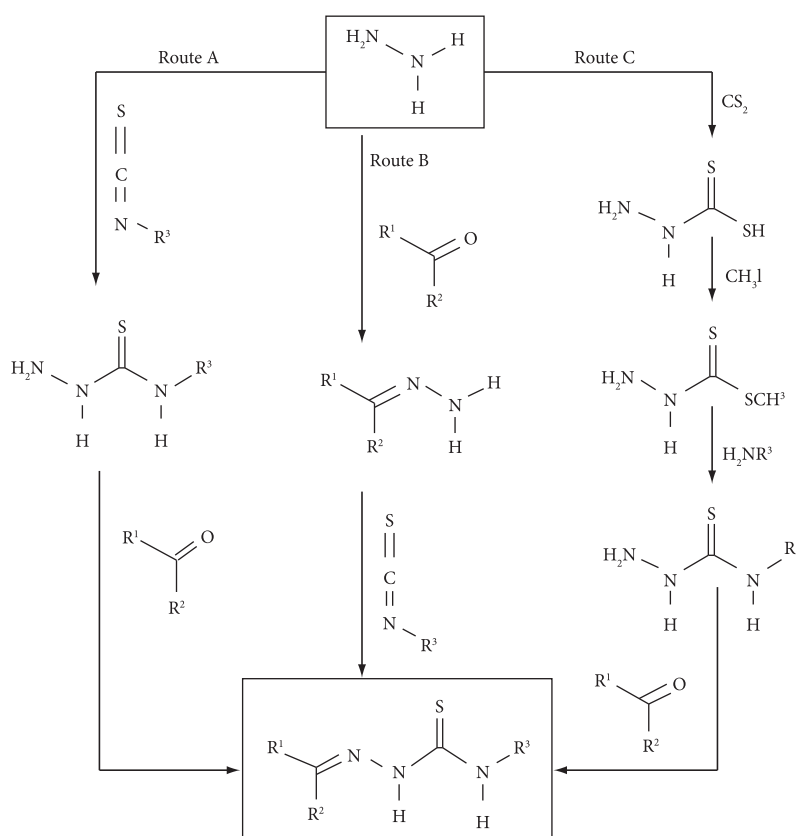


Figure 1. Routes to thiosemicarbazones.

to Scheme 1. In this condition compound 4a was obtained in good yield. We disclose herein our results concerning the first one-pot, catalyst-free synthesis of thiosemicarbazones via multicomponent coupling reactions of hydrazine, isothiocyanates and oxo compounds.

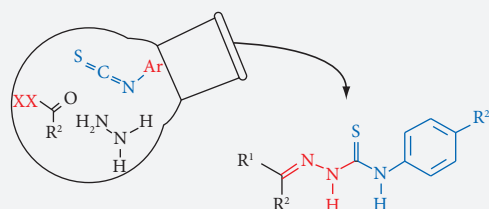


Figure 2. Multicomponent route to thiosemicarbazones.

In a typical synthetic procedure, equimolar amounts of isothiocyanate, hydrazine, and aldehyde or ketone in MeOH as solvent were heated under reflux at the indicated time (Figure 2).

With this optimal condition in hand, we extended the reaction to other oxo compounds, and results are indicated in Figure 3. A representative spectrum of monosubstituted and disubstituted aldehydes afforded thiosemicarbazones from modest to excellent isolated yields. The method is also useful for heteroaromatic and α,β -unsaturated aldehydes, and to some aromatic ketones.

In conclusion, this study shows that three-component coupling reaction involving isothiocyanates, hydrazine and oxo compounds can

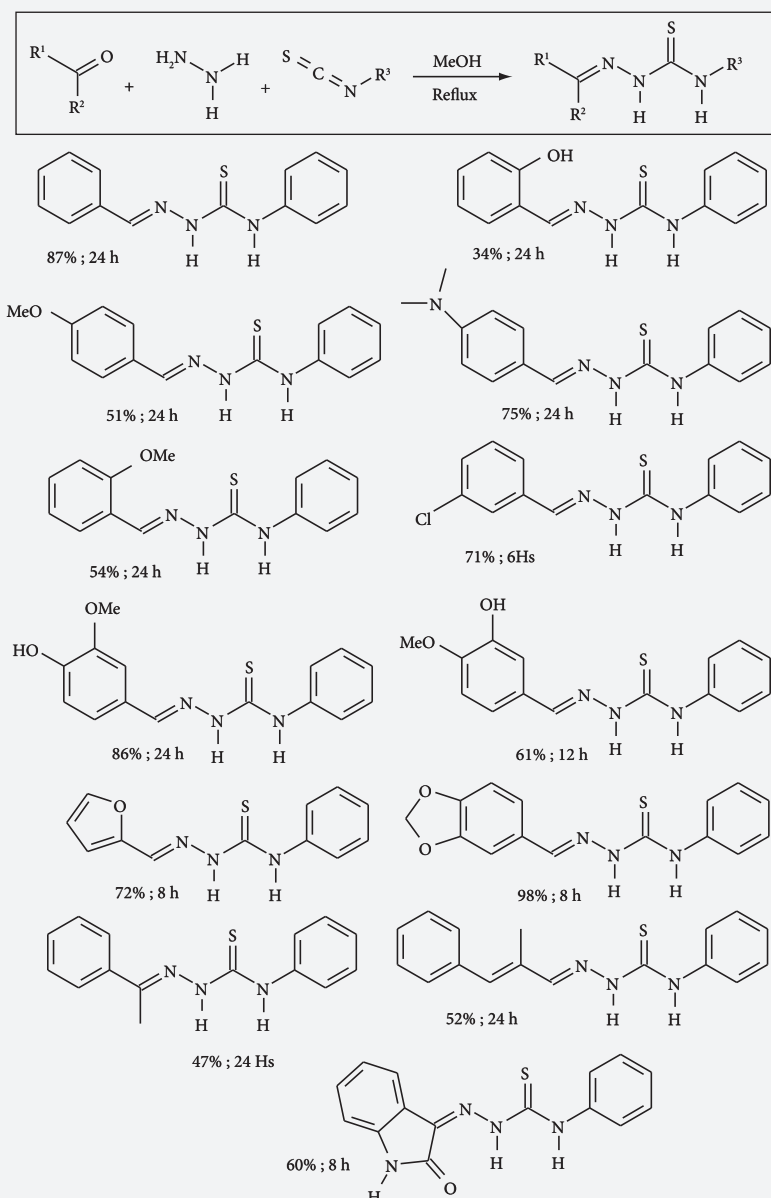


Figure 3. Obtained thiosemicarbazones

be conveniently employed as a direct, catalyst-free synthetic route to a broad spectrum of thiosemicarbazones. Since the experimental conditions are extremely simple, inexpensive, and very mild, we hope that this approach would be useful in the context of synthesis of molecular library for pharmacological applications. A novel and efficient procedure for the synthesis of thiosemicarbazones has been achieved via a multicomponent and catalyst-free reaction of phenyl or p-chlorophenyl isothiocyanate, hydrazine and aldehydes or ketones. The method afforded thiosemicarbazones in good yields and short reaction time.



Figure 4. Researches involved with this scientific project.

REFERENCES

1. HUDLICKÝ, T., REED, J. W., 2007. *The Way of Synthesis*, Wiley-VCH, 2007.
2. SCHREIBER, S. L., 2000. Target-oriented and diversity-oriented organic synthesis in drug discovery. *Science* 287, 1964-1969.
3. DOMLING, A., 2006. Recent Developments in Isocyanide Based Multicomponent Reactions in Applied Chemistry. *Chem. Rev.* 106, 17-89.
4. FISK, J.S., MOSEY, R.A., TEPE, J.J., 2007. The diverse chemistry of oxazol-5-(4H)-ones. *Chem. Soc. Rev.* 36, 1432-1440.
5. SPANDL, R.J., BENDER, A., SPRING, D.R., 2008. Diversity-oriented synthesis; a spectrum of approaches and results. *Org. Biol. Chem.* 6, 1149-1158.
6. SPRING, D.R., 2003. Diversity-oriented synthesis; a challenge for synthetic chemists. *Org. Biol. Chem.* 1, 3867-3870.
7. LO, M.M.-C., NEUMANN, C.S., NAGAYAMA, S., PERLSTEIN, E.O., SCHREIBER, S.L., 2004. A library of spirooxindoles based on a stereoselective three component coupling reaction. *J. Am. Chem. Soc.* 126, 16077-16086.
8. BERALDO, H., 2004. Semicarbazonas e tiossemicarbazonas: perfil farmacológico e usos clínicos. *Quim. Nova* 27, 461-471.
9. BERALDO, H.; GAMBINO, D., 2004. The wide pharmacological versatility of semicarbazones, thiosemicarbazones and their metal complexes. *Mini-Rev. Med. Chem.* 4, 31-39.
10. ALY, A.A., HASSAN, A.A., AMEEN, M.A., 2008. Chemistry of Cyclopropanones: Synthesis of New Pyrrolo[2,1-b]-1,3,4-oxadiazoles. *Tetrahedron Lett.* 49, 4060-4062.
11. AQUINO, T.M., LIESEN, A.P., SILVA, R.E.A., LIMA, V.T., CARVALHO, C.S., FARIA, A.R., ARAUJO, J.M., LIMA, J.G., ALVES, A.J., MELO, E.J.T., GOES, A.J.S., 2008. Synthesis, anti-Toxoplasma gondii and antimicrobial activities of benzaldehyde 4-phenyl-3-thiosemicarbazones and 2-[(phenylmethylene)hydrazono]-4-oxo-3-phenyl-5-thiazolidineacetic acids. *Bioorg. Med. Chem.* 16, 446-456.
12. For analysis of the problem of stop-and-go synthesis, see: WALJI, A.M., MACMILLAN, D.W.C., 2007. Strategies to Bypass the Taxol Problem. *Enantioselective Cascade Catalysis, a New Approach for the Efficient Construction of Molecular Complexity.* *Synlett*, 1477-1498.

LESSONS FROM THE TERRA PRETA DE ÍNDIOS OF THE AMAZON REGION FOR THE UTILIZATION OF CHARCOAL FOR SOIL AMENDMENT**

Etelvino H. Novotny,^a Michael H. B. Hayes,^b Beáta E. Madari,^c
Tito J. Bonagamba,^d Eduardo R. deAzevedo,^d André A. de Souza,^d Guixue Song,^e
Christiane M. Nogueira^f and Antonio S. Mangrich*,^g

^aEmbrapa Solos, Rua Jardim Botânico 1024, 22460-000, Rio de Janeiro-RJ, Brazil

^bChemical and Environmental Sciences, University of Limerick, Ireland

^cEmbrapa Arroz e Feijão, CP 179, 75375-000, Santo Antônio de Goiás-GO, Brazil

^dInstituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970, São Carlos-SP, Brazil

^eDepartment of Civil, Environmental, and Sustainable Engineering, Ira A. Fulton School of Engineering, Arizona State University, PO Box 875306, Tempe, AZ 85287-5306 USA

^fDepartamento de Química Orgânica, Instituto de Química, Universidade Federal Fluminense, 24020-150, Niterói-RJ, Brazil

^gDepartamento de Química, Centro Politécnico, Universidade Federal do Paraná, CP 19081, 81531-990, Curitiba-PR, Brazil

*e-mail: mangrich@quimica.ufpr.br

**see more at: NOVOTNY, E.H., et al. *Journal of the Brazilian Chemical Society* 2009, 20, 1003.

Many soils of the Amazon Region are highly weathered, acidic, with low fertility and low crop production potential. Soil fertility is the limiting factor for the sustainable agriculture in the Region. The Terra Preta de Índios (TPI) soils contrast with other Amazonian soils, especially in relation to fertility. TPI are soils that have an archeo-anthropogenic horizon. This is a surface horizon of variable depth, enriched in organic matter and containing pieces of ceramic and other evidence of human activity¹ (Figure 1). TPI soils occur in small patches, many of which do not exceed 2 ha, although areas of up to 350 ha have been reported. Currently it is accepted that the TPI are of pre-Columbian origin, the result of activities of indigenous peoples, although it is unclear whether

it is a result of an intentional process of improving the soil, or the consequence of agricultural and domestic activities of these peoples.

Human activity in the pre-Columbian past has resulted in the accumulation of plant and animal residues, as well as large quantities of ash, charcoal, and various chemical elements, such as P, Mg, Zn, Cu, Ca, Sr and Ba, representing the geochemical signature of human occupation². These accumulations probably contributed decisively to the formation of fertile soils, with higher pH, Ca and Mg, P, cation exchange capacity (CEC) and base saturation, compared with the adjacent non anthropogenic soils (Table 1).

The high fertility of the TPI, and in particular its resilience (the capacity of these soils to maintain



Figure 1. Photographs of TPI profiles and of ceramic artifacts found in these soils.

high fertility in spite of its intensive and degradative use), is attributed to the high levels of soil organic matter and to the physical and chemical properties of this organic matter. These soils have a carbon content of up to 150 g/kg of soil, compared with 20-30 g/kg in adjacent soils³. Additionally, the enriched layer of carbon can be up to 200 cm deep, with an average depth of the order of 40-50 cm, whereas the carbon in the adjacent soils is limited to the top 10-20 cm. Thus, the stock of carbon in the TPI may be an order of magnitude higher, and can be up to six times more stable than that in adjacent soil. This material is highly resistant to thermal-, chemical- and photo-oxidation, and due to its recalcitrance, its incorporation into the soil is an important and efficient mechanism of carbon sequestration.

However, the partial oxidation of the aromatic peripheral units produces carboxylic and others organic functional groups directly linked to the recalcitrant aromatic structures (Figures 2a, 2b and A). The organic functional groups, additionally to its recalcitrant aromatic structure ensure the sustainability and resilience of TPI.

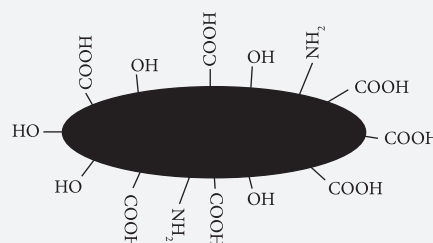


Figure A. Soil organic matter pictorial chemically inert core and reactive periphery⁴.

Table 1. Chemical attributes of soils of the Amazon Region

Soils	pH	Ca + Mg ^a	CEC	P ^b	Base saturation ^c %
		(cmolc kg ⁻¹)			
Control	4.4	1.3	9.5	5	21
TPI	5.4	6.8	17.3	300	55

^a exchangeable; ^b mehllich; ^c base saturation = (Ca + Mg + K) / CEC.

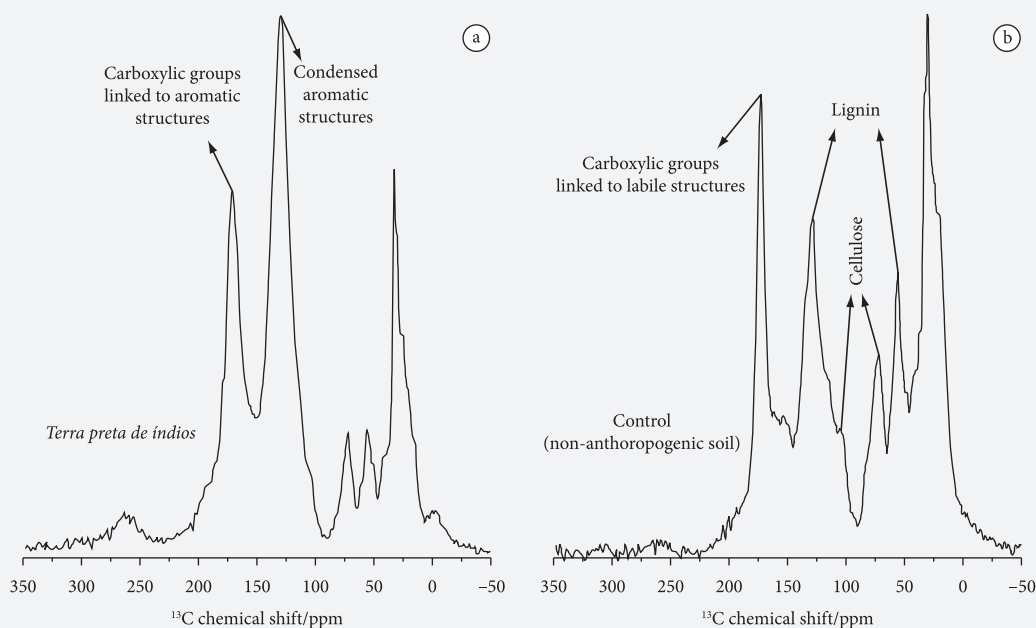


Figure 2. ¹³C-NMR spectra of humic acids from Amazon region soils. (a) TPI; (b) Non-anthropogenic soil.

REFERENCES

- WOODS, W.I., DENEVAN, W.M. In Amazonian Dark Earths: Wim Sombroek's Vision; WOODS, W.I., TEIXEIRA, W.G., LEHMANN, J., STEINER, C., WINKLERPRINS, A., REBELLATO, L., eds.; Springer Science: Heidelberg, 2009, ch. 1.
- DA COSTA, M.L., KERN, D.C., 1999. Geochemical signatures of tropical soils with archaeological black earth in the Amazon, Brazil. *J. Geochem. Explor.* 66, 369-385.
- GLASER, B., HAUMAIER, L., GUGGENBERGER, G., ZECH, W., 2001. The Terra Preta phenomenon - a model for sustainable agriculture in the humid tropics. *Naturwissenschaften* 88, 37-41.
- MANGRICH, A.S., 2009. R&D Trends on Biofuels in Brazil With the Focus on New Biofuels Technologies. In German-Brazilian Workshop on Biodiesel and New Biofuels. Berlin, GE, 01./02. December 2009.

DETERMINATION OF TRACE ELEMENTS IN CRUDE OIL AND IN BIOLOGICAL AND GEOLOGICAL SAMPLES BY ATOMIC SPECTROMETRY**

Daniel L. G. Borges, Vera L.A. Frescura and Adilson J. Curtius

Laboratório de Espectrometria Atômica, Departamento de Química,
Universidade Federal de Santa Catarina – UFSC, 88044-900, Florianópolis, SC, Brazil
*e-mail: curtius@qmc.ufsc.br

**see more at: DITTERT, I.M., *et al. Spectrochimica Acta. Part B, Atomic Spectroscopy* 2009, 64, 537;
DITTERT, I.M., *et al. Microchimica Acta* 2009, 167, 21-26; SANTOS, E.J., *et al. Spectrochimica Acta Part B, Atomic Spectroscopy* 2009, 64, 549; TORRES, D.P., *et al. Journal of Analytical Atomic Spectrometry* 2009, 24, 1118; TORRES, D.P., *et al. Microchemical Journal* 2009, 93, 206; NARDI, E., *et al. Food Chemistry* 2009, 112, 727;
BATISTA, B.L., *et al. J. Braz. Chem. Soc.* 2009, 20, 1406; BORGES, D.L.G., *et al. Analytical Chemistry* 2009, 81, 9834.

The Laboratório de Espectrometria Atômica of UFSC had the opportunity to propose several experimental procedures for the determination of trace elements in different samples that resulted in published papers in 2009. Some of the publications will be briefly discussed in the following paragraphs.

A direct, sensitive and fast method for the simultaneous determination of Cr and Fe in crude oil using high resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) was proposed.¹ In the HR-CS AAS, the use of a continuum source, a double monochromator with high resolution, and a UV-sensitive CCD detector make possible the visualization of the entire spectral environment at about ± 0.250 nm in the vicinity of the analytical line, allowing the simultaneous determination of elements which have absorption lines within this spectral interval. The measurements were carried out at the main Cr line, 357.868 nm, and at a secondary Fe line, 358.120 nm, using optimized pyrolysis and atomization temperatures. For the verification of the accuracy, two certified reference oil samples were analyzed and the results were in agreement with the certified or informed values. External calibration with aqueous standard solutions. was adequate. In Figure 1, the 3D spectrum of a crude oil sample is shown, indicating absence of spectral interference on the analytical peaks. Five crude oils samples were analyzed. The obtained concentrations were in the ranges from 4.1 to 173.2 ng g⁻¹ for Cr and from 2.2 to 4.4 μ g g⁻¹ for

Fe. The precision expressed as the relative standard deviation, varied from 6 to 20% for Cr and 4 to 16% for Fe, being acceptable for the direct analysis of complex samples.

The same analytical technique, HR-CS AAS, was also used for the direct determination of silver in geological samples.² Pyrolysis and atomization temperatures were optimized as 800 °C and 1900 °C, respectively, for soils and sediments, and calibration against aqueous standards resulted in good agreement between certified or informed values and determined values at a 95% confidence level. The analysis of rocks and ores, however, required calibration against a solid certified reference rock sample, as in these samples the sulfur-rich matrix reduces the atomization efficiency. For these

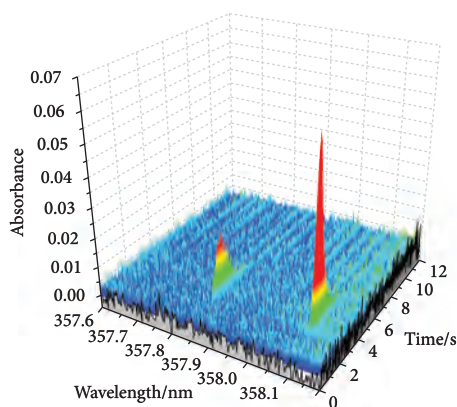


Figure 1. Time and wavelength-resolved absorbance spectrum for the crude oil “Crudo mediano-2” in the vicinity of the chromium line at 357.869 nm. Pyrolysis temperature of 1400 °C, atomization temperature of 2500 °C.

samples, background absorption with pronounced fine structure due to a sulfur-containing molecule was detected, although with negligible influence on the analytical signal at the optimized atomization temperature of 2300 °C. The application of a least-squares background correction algorithm resulted in a background-free sample spectrum, as shown in Figure 2. Ten certified samples were analyzed.

The analysis of biological samples has been the subject of several publications.³⁻⁷ A simple and fast method for the determination of Se in biological samples, including food, by axial view inductively coupled plasma optical emission spectrometry using on-line chemical vapor generation (CVG-ICP OES) from the samples pre-treated with aqua regia under microwaves followed by sonication was proposed.³ Selenium may act as an essential nutrient or as a toxin, depending on its concentration and on its chemical form. The concentrations of HCl and NaBH₄, used in the chemical vapor generation were optimized by factorial analysis. Six certified materials were treated with 10 mL of aqua regia in a microwave system under reflux for 15 min, followed

by additional 15 min in an ultrasonic bath. After dilution, Se was determined directly by CVG-ICP OES, using the analytical line at 196.026 nm. External calibration against aqueous standards in 10% v/v aqua regia was adequate. The experimental part of this work was carried out at Tecpar, Curitiba.

Two papers on mercury fractionation in biological samples were published. A simple, fast and reliable method for the determination of inorganic and total mercury in biological samples directly from slurries prepared in water has been developed using cold vapor atomic absorption spectrometry.⁴ Samples were simply mixed with water and measurement were carried out immediately. For inorganic mercury determination, no additional preparation was required. For total mercury determination, the samples had to be oxidized previously with a 2% m/v KMnO₄ solution for 2 min. After this period, the measurements were carried out similarly to that for inorganic mercury determination. The methylmercury concentration could then be calculated as the difference between total and inorganic mercury. The results were in

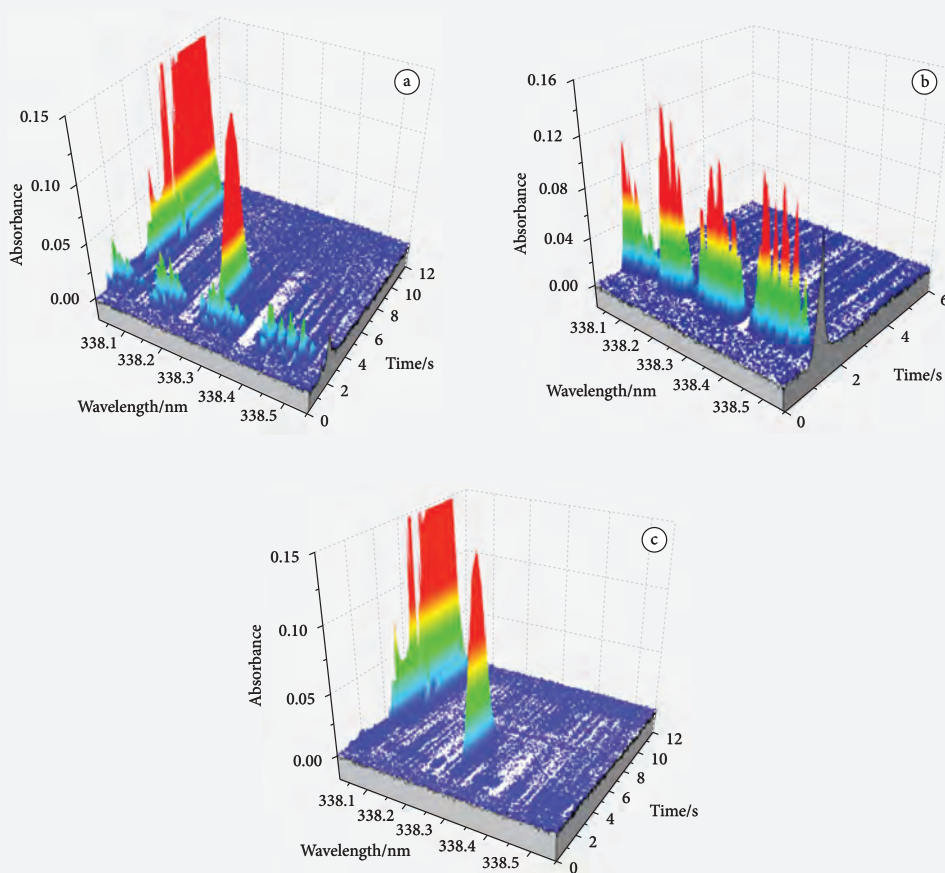


Figure 2. Time and wavelength-resolved absorbance spectra in the vicinity of the Ag line at 338.289 nm: a) spectrum of the WMS-1 rock sample; b) reference spectrum of the sulphur-containing molecule; c) WMS-1 spectrum obtained after least-squares background correction.

good agreement with the 95% confidence level of the certified or close to the informed value for the four reference materials investigated, as shown in Table 1. The relative standard deviation was better than 7% for most of the samples. The limits of detection in the sample were determined as 0.020 and 0.016 $\mu\text{g g}^{-1}$ for inorganic and total mercury, respectively.

In the other paper⁵, after the CRM treatment at room temperature with tetramethylammonium hydroxide (TMAH), inorganic mercury was determined by CV AAS. Total mercury was measured by the same technique, following microwave-assisted acid digestion. Organic mercury, basically methylmercury, was obtained by difference. In both procedures, the quartz tube was kept at room temperature. The difference between the total and inorganic mercury concentrations agreed with the methylmercury concentration for the four certified

materials investigated. A single calibration curve against aqueous standards in acidic medium was carried out for both procedures. The limits of detection in the samples were 0.02 $\mu\text{g g}^{-1}$ and 0.04 $\mu\text{g g}^{-1}$ for inorganic and total Hg, respectively, since the sample mass for total mercury was half of that for inorganic mercury determination. Simplicity and high efficiency without using chromatographic techniques are some of the qualities of the proposed method, turning it into an interesting alternative for the fractionation analysis of mercury in biological samples.

Two other papers involving the analysis of food⁶ and urine⁷ were developed in collaboration with researchers from FCFRP-USP. Another work, involving the direct determination of organometallic compounds by ambient mass spectrometry detection was carried out at NRCC, in Canada, in another collaborative study.⁸

Table 1. Analytical results for the determination of total, inorganic and methylmercury in certified reference materials by CV AAS using slurry preparation in water (inorganic Hg) or after addition of KMnO_4 (total Hg). Obtained values (mean \pm confidence limit) in $\mu\text{g g}^{-1}$; n = 3 or 4.

Sample	Total mercury		Methylmercury (as Hg)		Inorganic mercury	
	Certified	Found	Certified	Found ^a	Informed ^b	Found
BCR 186	1.97 \pm 0.04	2.01 \pm 0.22	NC	0.70 \pm 0.08	1.5 \pm 0.1	1.30 \pm 0.14
DOLT-3	3.37 \pm 0.14	3.51 \pm 0.19	1.59 \pm 0.12	1.65 \pm 0.04	1.78	1.86 \pm 0.19
TORT-2	0.27 \pm 0.06	0.28 \pm 0.03	0.152 \pm 0.013	0.148 \pm 0.009	0.118	0.135 \pm 0.021
ERM-CE 278	0.196 \pm 0.009	0.193 \pm 0.031	NA	ND	NA	< LOQ

^a Calculated as the difference between total Hg and inorganic Hg. ^b Calculated as the difference between total Hg and Hg as CH_3Hg^+ . NA: not available. ND: not determined.

REFERENCES

- DITBERT, I.M., SILVA, J.S.A., ARAÚJO, R.G.O., CURTIUS, A.J., WELZ, B., BECKER-ROSS, H., 2009. Direct and simultaneous determination of Cr and Fe in crude oil using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Spectrochimica Acta. Part B, Atomic Spectroscopy* 64, 537-543.
- DITBERT, I.M., BORGES, D.L.G., WELZ, B., CURTIUS, A.J., BECKER-ROSS, H., 2009. Determination of silver in geological samples using high-resolution continuum source electrothermal atomic absorption spectrometry and direct solid sampling. *Microchimica Acta* 167, 21-26.
- SANTOS, E.J., HERRMANN, A.B., DECAIRES, S., FRESCURA, V.L.A., CURTIUS, A.J., 2009. Determination of Se in biological samples by axial view inductively coupled plasma optical emission spectrometry after digestion with aqua regia and on-line chemical vapor generation. *Spectrochimica Acta Part B, Atomic Spectroscopy* 64, 549-553.
- TORRES, D.P., BORGES, D.L.G., FRESCURA, V.L.A., CURTIUS, A.J., 2009. A simple and fast approach for the determination of inorganic and total mercury in aqueous slurry of biological samples using cold vapor atomic absorption spectrometry and in situ oxidation. *Journal of Analytical Atomic Spectrometry* 24, 1118-1122.
- TORRES, D.P., FRESCURA, V.L.A., CURTIUS, A.J., 2009. Simple mercury fractionation in biological samples by CV AAS following microwave-assisted acid digestion or TMAH pre-treatment. *Microchemical Journal* 93, 206-210.
- NARDI, E., EVANGELISTA, F., TORMEN, L., SAINTPIERRE, T.D., CURTIUS, A.J., SOUZA, S., BARBOSA JR, F., 2009. The use of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of toxic and essential elements in different types of food samples. *Food Chemistry* 112, 727-732.
- BATISTA, B.L., RODRIGUES, J.L., TORMEN, L., CURTIUS, A.J., BARBOSA JR, F., 2009. Reference concentrations for trace elements in urine for the Brazilian population based on q-ICP-MS with a simple dilute-and-shoot procedure. *Journal of the Brazilian Chemical Society* 20, 1406-1413.
- BORGES, D.L.G., STURGEON, R.E., WELZ, B., CURTIUS, A.J., MESTER, Z., 2009. Ambient mass spectrometric detection of organometallic compounds using direct analysis in real time. *Analytical Chemistry* 81, 9834-9839.

QUANTIFICATION AND SOURCE IDENTIFICATION OF ATMOSPHERIC PARTICULATE POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR DRY DEPOSITION FLUXES AT THREE SITES IN SALVADOR BASIN, BRAZIL, IMPACTED BY MOBILE AND STATIONARY SOURCES**

Gisele Olimpio da Rocha^{1,2}, Wilson Araujo Lopes¹, Pedro Afonso de Paula Pereira^{1,2}, Pérola de Castro Vasconcelos³, Fábio Souza Oliveira⁴, Luiz Souza Carvalho¹, Liliâne dos Santos Conceição¹, Jailson Bittencourt de Andrade^{1, 2,*}

¹ Instituto de Química – UFBA, Campus de Ondina, 40170-115, Salvador – BA, Brazil

² Centro Interdisciplinar de Energia e Ambiente – CIEnAm, UFBA, 40110-040, Salvador – BA, Brazil

³ Instituto de Química, Universidade de São Paulo – USP, Cidade Universitária- Butantã, 05508-900, São Paulo – SP, Brazil

⁴ Universidade Federal do Recôncavo da Bahia – UFRB, Centro de Ciências da Saúde, Santo Antônio de Jesus – BA, Brazil

*e-mail: jailsong@ufba.br

**see more at: DA ROCHA G.O., et al. J. Braz. Chem. Soc. 2009, 20, 680.

Particulate matter plays a significant role in the chemistry of the atmosphere and in human health. While their constitution may vary from place to place, the sources of particulate matter are numerous, from natural origin – mainly vegetation and dust resuspension, among others – to different kinds of human activities, such as disposal of petroleum residues, waste incineration, energy production, vehicular emissions and agricultural slash burning. Vehicle exhaust aerosols contain carbonaceous particles that are associated with a complex mixture of compounds. Special attention has been given to particles emitted by diesel engines, due to the numerous *in vivo* and *in vitro* studies establishing their adverse effects in human health. Among the several organic and inorganic species which are associated with diesel exhaust particles, including mono- and poly- functional organic compounds resulting from gas-to-particle conversion mechanisms, hydrocarbons with high molecular weight, such as polycyclic aromatic hydrocarbons (PAH) and their oxy- and nitro-derivatives, are of particular interest. PAH are ubiquitous and abundant pollutants that are emitted from several natural and/or anthropic sources and may be present in the atmosphere, hydrosphere and lithosphere. The

widespread occurrence of PAH is largely due to their formation and emission during incomplete combustion of petrogenic materials such as oil and coal as well as non-petrogenic sources as wood burning as well as biomass burning due to agricultural practices.¹ In urban areas, exhausts from diesel and gasoline vehicles play an important role to the PAH emissions. Many PAH are regarded as priority pollutants by both the United States Environmental Protection Agency and the European Community. While no standard currently exists in Brazil for PAH concentrations in ambient air, the U.K. Government Expert Panel on Air Quality Standards is considering an air quality standard for PAH of 0.25 ng m⁻³ (annual mean), to be achieved on December 2010².

The aim of the present work was to determine the atmospheric concentrations and profiles of 16 particle-phase US EPA priority PAH pollutants, present in the same three sites previously studied, namely: i) Lapa Bus Station, strongly impacted by heavy-duty diesel vehicles; ii) Aratu Harbor, impacted by an intense movement of goods, including metal ores and chemicals and near industrial centers and; iii) Bananeira Village, located on Maré Island, a non vehicle-influenced

site, with activities such as handcraft work and fishery, although placed near the port³.

The Lapa Bus Station is placed in downtown Salvador City in a region featured by heavy commerce and service activities. The station is composed of three floors: the first one being located on underground level, and the second at the ground level, with total areas of about 13,920 m², each one has 5 platforms for arrivals and departures of urban heavy-duty diesel buses, and the third floor is occupied by small stores, cafeterias and the administration services. Samples ($n = 36$) of PM₁₀ were collected between 16-28 July 2005 on quartz filters (22.8 × 17.7 cm, Energética, RJ, Brazil) by using a PM₁₀ Hi-Vol sampler (Energética, RJ, Brazil and Thermo Andersen, USA) on the bus platform from underground floor. Sampling periods were either 4-6 h during morning/afternoon and 8-10 h during the night (along weekdays) or 24 h (during weekends) under average sampling flow rate of 1.14 m³ min⁻¹.

Aratu Harbor, in Todos os Santos Bay, about 50 km far away of Salvador, possess about 60% of total operations in ports of the Salvador Region by supporting transportation of manufactures from both the Industrial Center of Aratu (CIA) and the Petrochemical Complex of Camaçari. Its average temperature is 26 °C and the predominant winds are NE (3-37%), E (3-52%) and SE (3-50%). In this semi-urban site, particles were simultaneously sampled in two size fractions: TSP ($d_p \leq 100 \mu\text{m}$) and PM₁₀ by locating the Hi-Vol samplers at average flow rates of 1.16 and 1.14 m³ min⁻¹, respectively, in two different points: firstly the Aratu#1 (7 samples), near an office building and secondly the Aratu#2 (8 samples), in an open place (Figure 1). The samples were collected from October to November 2004, in sampling periods of 24 hours each one.

Bananeira Village, in the Mare Island, located at Todos os Santos Bay, is a remote site in which fishery and handcraft activities dominate. This place, depending on the wind direction and other meteorological conditions, receives air masses



Figure 1. Map of Todos os Santos Bay locating the collecting sites.

(and also emissions) from an industrial center (CIA) and from the Petrochemical Complex of Camaçari and thus its *ca.* 1000 inhabitants may possibly suffer consequences of them. TSP samples ($n = 14$) of 24 h periods, by using a TSP Hi-Vol at a flow rate $1.16 \text{ m}^3 \text{ min}^{-1}$, were collected on September-October 2005.

Just after each sampling, filters were conserved in aluminum foil envelopes and inside sealed plastic bags until weighing and analysis. Either the extraction of the PAH from filters and GC-MS-SIM analyses were performed as described on *Pereira et al.* 2002⁴ and *Lopes et al.* 2008⁵, respectively. All of the EPA priority PAH was identified in samples of the four sites of this study. In all sites it can be observed that PAH with higher molecular weight and lower vapor pressure (those ones with 4-6 benzene rings, namely BaA, CRY, BbF, BkF, BaP, IND, DBA and BgP) reached higher particle phase concentrations and those with 2-3 rings such as NAP, ACY, ACE and FLU were fairly found. Nonetheless, considering all sampling days, BbF (ranging from 0.130 - 6.85 ng m^{-3}) is the PAH with the highest concentration in samples from Bananeira and Aratu Harbor as well as CRY (from 0.075 - 6.85 ng m^{-3}) presented higher concentrations in the Lapa Bus Station. PAH arithmetic mean concentrations were higher

in TSP than in PM_{10} , showing a similar PAH distribution in Aratu #1 and Aratu #2 in spite the fact that lower PAH concentration levels belonged to Aratu #2. This could be due to differences of the air masses trajectories of both places, as discussed elsewhere. Aratu Harbor, during sampling TSP and PM_{10} , has received in its terminals discharges of many kinds of goods, including coke, charcoal and petrol derivatives. Additionally, the diesel oil used to fuel the ships has probably contributed to the PAH content of this place. Bananeiras village, on the other hand, seems to be mainly a receptor site for emissions from the Industrial Center of Aratu. Contributions of carcinogenic species (BaA, BbF, BkF, BaP, DBA, and IND) for the PAH content represents (in $\mu\text{g g}^{-1}$) 42.4, 25.4, 78.2, 25.2, 79.4 and 45.3 for Aratu #1 TSP, Aratu #2 TSP, Aratu #1 PM_{10} , Aratu #2 PM_{10} , Bananeiras and Lapa, respectively. Figure 2 brings out relative contributions of both carcinogenic (to which BbF, BkF and BaP are the major contributors) and non-carcinogenic (major contributors are BgP, CRY, and PYR) PAH measured. In three sites amongst the four studied, the carcinogenic PAH represent the main fraction in the total PAH determined in particulate matter, with percentual values very similar (*ca.* 70 %), what should evidence serious health concerns. The only exception was the Lapa

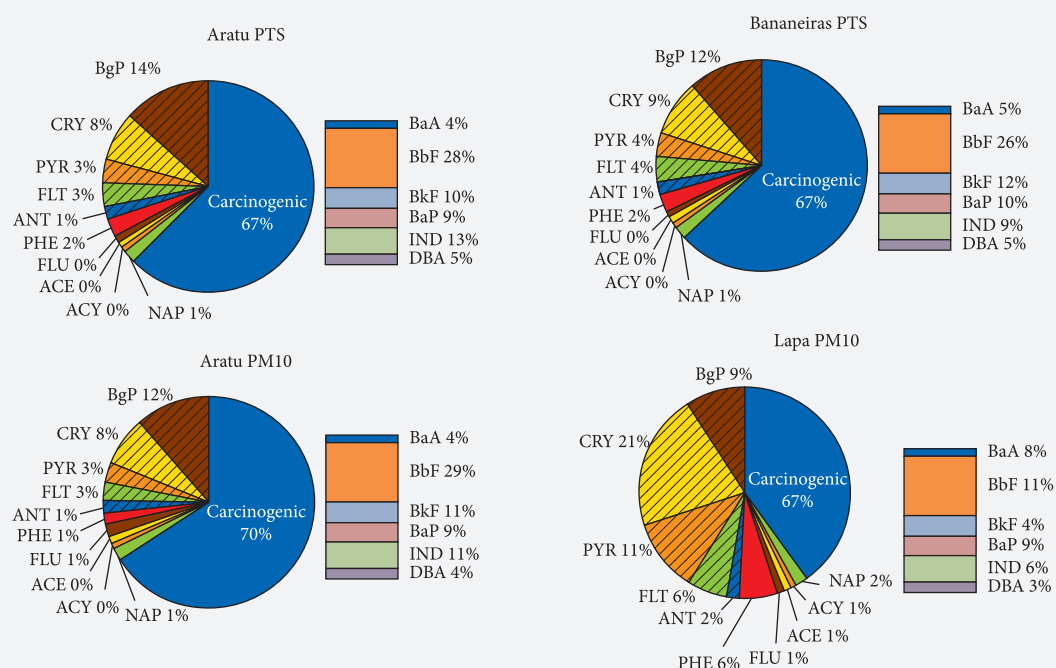


Figure 2. Percentage contributions of individual compounds, and carcinogenic species, to the total mass of measured PAH for each studied site.

Station, where carcinogenic PAH just accounted for 40% of the total PAH.

The main reason for this was that the Lapa station had only 21% of those carcinogenic BbF, BkF and IND, against about 50% in Aratu and Bananeiras. On the other hand, non-carcinogenic CRY and PYR accounted for 31% of the total PAH in Lapa, against only 12 % in Aratu and Bananeiras. The PAH mean concentrations in PM₁₀ from Lapa Bus Station, according to the sampling day, are shown in Figure 3, as well as those according to sampling period are shown in Figure 4. Because circulation of commuting buses and people throughout Metropolitan Region of Salvador City is most intensified during 1 p.m. until 8 p.m. and between Monday and Friday, the emissions of particle-associated PAH reached their highest levels on weekdays and during afternoon, due to continued diesel burning in heavy-duty vehicles and particle resuspension associated to the traffic.

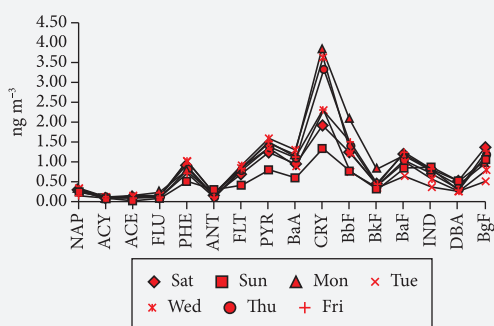


Figure 3. Comparison of mean PM₁₀ PAH concentrations at different days (each day represents a minimum of 3 values) from Lapa Bus Station.

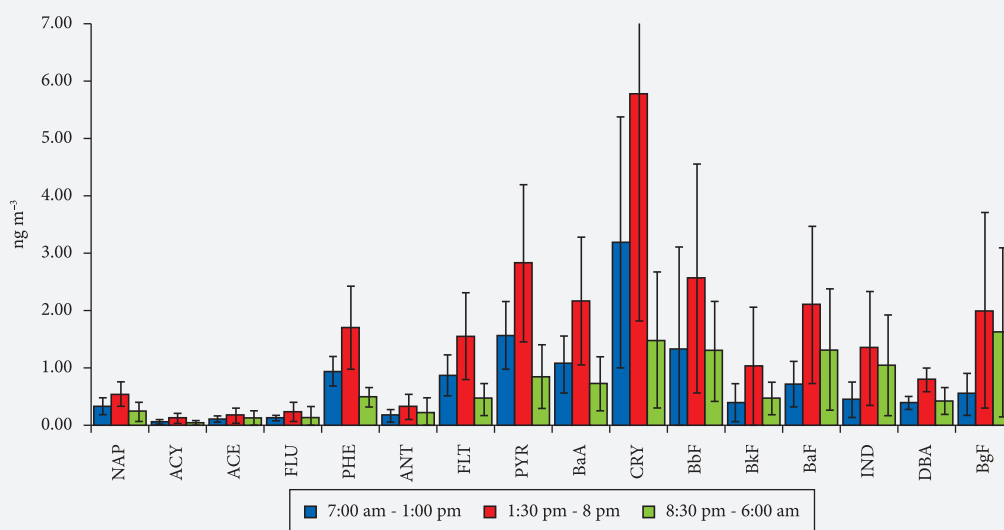


Figure 4. Contribution according to period of the day for PAH concentrations in Lapa Bus Station (PM₁₀).

In this work, we are tentatively associating PAH designed as “source tracer” to Pearson Correlation, Principal Component Analysis, Cluster Analysis, and Diagnostic ratios (Table 2) in order to propose the major PAH sources for each site. When considering Pearson correlations we have found, firstly, that both Aratu#1 and Aratu #2 TSP have shown two main correlation groupings: moderate-to-strong correlations among NAP, ACE, FLU, PHE and ANT ($0.44 < r < 0.70$) that could be representative of industrial emissions and/or petrol refinery from CIA and industrial complex of Camaçari; and strong correlations for FLT, PYR, BaA, CRY, BbF, BkF, BaP, IND, DBA and BgP ($0.70 < r < 1.00$) that may represent either gasoline or diesel emissions, although ACY, IND and BgP ($r > 0.81$) were well correlated in Aratu #1 TSP only. Secondly, Aratu #2 TSP ACY has correlated with the more volatile species NAP, ACE and FLU ($r > 0.59$). Aratu #1 and Aratu #2 PM₁₀ presented higher Pearson scores and more PAH species in correlation with one another. Here those heavier species shows again strong correlations among them (PYR, FLU, BaA, CRY, BbF, BkF, BaP, IND, DBA and BgP with $0.70 < r < 0.99$). In this site we tentatively try to attribute those correlations as industrial emissions and/or petrol refinery and gasoline or diesel emissions. Thirdly, Bananeiras shows two distinct correlation groups, the former with weak-to-moderate correlations among NAP, ACY, ACE, FLU, PHE, and ANT ($0.37 < r < 0.58$, what could be petrol refinery, wood combustion

for domestic heating/energy production) and the latter with moderate-to-strong correlations among FLT, PYR, BaA, CRY, BbF, BkF, BaP, IND, DBA and BgP ($0.81 < r < 0.96$, diesel exhausts from boats). Finally, Pearson correlations from Lapa Station have shown the lowest score values and the least species involved into correlations of all sites. This could denote more PAH sources on that site, which would reflect into more difficult correlations between them, since more than one or two different sources should be participating of the origin of each PAH. In this site there are weak-to-moderate inter-correlations between NAP, ACY, ACE, FLU, PHE, FLT, PYR and BaA ($0.15 < r < 0.84$) and also moderate-to-strong correlations among PHE, FLT, PYR, CRY, BbF, BkF, BaP, IND, DBA and BgP ($0.51 < r < 0.99$ diesel exhausts from heavy-duty vehicles). PCA analysis shows that the first principal component explains 60% and the second accounts for 30 % of all variance data, distinguishing two main groups according to similarities in the PAH emission patterns: the first group, formed by Aratu (#1 and #2 as well as TSP and PM_{10}) and Bananeiras (TSP), and the second group, formed by samples from Lapa Station.

Compared to Lapa Station samples, Aratu and Bananeiras samples would be expected to have both relatively high concentrations of those

compounds with positive loadings (BbF, DBA, BkF, IND, BgP, and BaP) on the first principal components and low concentrations of some other compounds with negative loadings (NAP, ACE, ACY, and FLU). Furthermore, Lapa samples have shown high concentrations and positive loadings for the second principal components (BgP, BaP, and BbF) and both highly concentrations and negative loadings for the second principal components (PHE, FLT, BaA, PYR, and CRY). Table 1 compares the PAH ratios of this study with those reported by other researchers. Firstly, the FLT/PYR, BaA/CRY, FLT/(FLT+PYR), BaA/(BaA + CRY), IND/(IND + BgP) ratios can be indicative of either gasoline exhaust from light-duty vehicles, diesel fuel burning on ships and from trucks, and coke discharge for Aratu #1 TSP, Aratu #2 TSP, Aratu #1 PM_{10} , and Aratu #2 PM_{10} . (BbF+BkF)/BgP seems to be a signature of domestic soot for samples of both fractions of PM from Aratu Harbor and Bananeiras, while for Lapa station it points out for vehicles or diesel exhaust. Secondly, FLT/PYR (0.94) and FLT/(FLT + PYR) (0.48) for Bananeiras shows wood combustion (for energy production and slash clearance) source; BgP/IND (1.2), BaP/BgP (0.88), IND/(IND + BgP) (0.45) are either coal combustion or diesel fuel burning on ships and boats. Finally, the following ratios BgP/

Table 1. PAH Diagnostic ratios for this study, and for different sources.

	FLT/ PYR	(BbF+BkF)/ BgP	BgP/ IND	BaP/ BgP	BaA/ CRY	PYR/ BaP	FLT/ (FLT+PYR)	BaA/ (BaA+CRY)	IND/ (IND+BgP)
Sites ^a									
Aratu #1 TSP	0.88	3.0	1.1	0.72	0.48	0.32	0.47	0.32	0.49
Aratu #2 TSP	0.94	2.5	1.1	0.60	0.43	0.29	0.49	0.30	0.47
Aratu #1 PM_{10}	1.0	3.2	1.1	0.73	0.51	0.34	0.50	0.34	0.48
Aratu #2 PM_{10}	0.87	2.4	1.1	0.60	0.50	0.37	0.47	0.33	0.47
Bananeira TSP	0.94	3.2	1.2	0.88	0.53	0.38	0.48	0.35	0.45
Lapa Bus Station PM_{10}	0.55	1.7	1.5	1.0	0.38	1.3	0.36	0.28	0.4
Reported sources									
Vehicles		0.20-1.72	1.0-2.7	0.3-0.78	0.63				
Gasoline exhaust	<1.0	0.33	3.5-3.8	0.3-0.4	0.28-1.2	0.85	0.43	0.37	0.18
Diesel exhaust		1.6	1.1-1.2	0.46-0.81	0.17-0.36	0.81		0.45	0.46
Wood combustion	1				0.93	0.71	0.56-0.67	0.48-0.54	0.58-0.69
Rice straw combustion			0.67	2					0.64
Coal combustion	1.4		1.1	0.9-6.6	1.0-1.2				
Coke oven				5.1	0.7				
Incinerators				0.14-0.60					
Petroleum refining				0.65-1.7					
Domestic soot		1.5-14.0							

IND (1.5), (BbF + BkF)/BgP (1.7), BaP/BgP (1.0), BaA/CRY (0.38), BaA/(BaA + CRY) (0.28), and IND/(IND + BgP) (0.40) are broad signatures of diesel heavy-duty vehicles for Lapa Station.

Dry atmospheric deposition fluxes (F_d) were calculated by multiplying the geometric mean of each PAH concentration (C_i) in the particulate matter to PAH dry settling velocity (V_d)⁶. Indeed, some authors have modeled V_d , and they have found results comparable to those from In this study PAH particle dry deposition were calculated by using V_d stated on *Sheu et al., 19967*.

Dry deposition flux for the total PAH (F_d of PAH) showed the highest value (4.35 $\mu\text{g m}^{-2} \text{day}^{-1}$) for Lapa Bus Station, followed by Aratu #2 TSP (3.69 $\mu\text{g m}^{-2} \text{day}^{-1}$), Aratu#1 TSP (2.96 $\mu\text{g m}^{-2} \text{day}^{-1}$) and Aratu #1 PM10 (2.93 $\mu\text{g m}^{-2} \text{day}^{-1}$), Bananeiras (2.49 $\mu\text{g m}^{-2} \text{day}^{-1}$), and Aratu #2 PM10 (1.95 $\mu\text{g m}^{-2} \text{day}^{-1}$).

Individual deposition fluxes are found in Table 2. In most sites BbF was the PAH with the highest deposition flux followed by BgP and IND. Exception is made for Lapa Station where CRY, BgP, BaP and BbF demonstrated higher F_d loadings. The apparent dry deposition fluxes took into account both the geometric averaged concentration level of an individual PAH sorbed on particulate matter and dry deposition velocity but it should also be taken into account the PAH reactivity which can be an important parameter in interpreting the dataset. *Nielsen (1984)*⁸ has developed a reactivity scale that groups PAH into five classes of reactivity (from Class I – the most reactive group – to Class V – the least reactive ones) toward nitrating species generating then either nitro-PAH, oxy-PAH or quinones (these are PAH derivatives much more carcinogenic

Table 2. Estimates of particle PAH dry deposition fluxes (F_d).

	PYR	BaA	CRY	BbF	BkF	BaP	IND	DBA	BgP
Dry settling velocity (V_d) (cm s ⁻¹)*	0.2	0.35	0.54	0.55	0.62	0.71	0.89	0.76	0.97
Aratu#1 TSP									
Geometric mean (ng m ⁻³)	0.286	0.299	0.714	2.44	0.820	0.732	1.01	0.363	1.02
Dry deposition flux (F_d) ($\mu\text{g m}^{-2} \text{day}^{-1}$)	0.05	0.09	0.33	1.16	0.44	0.45	0.78	0.24	0.85
Aratu#2 TSP									
Geometric mean (ng m ⁻³)	0.157	0.201	0.419	1.43	0.537	0.476	0.671	0.237	0.759
Dry deposition flux (F_d) ($\mu\text{g m}^{-2} \text{day}^{-1}$)	0.03	0.06	0.20	0.68	0.29	0.29	0.52	0.16	0.64
Aratu#1 PM10									
Geometric mean (ng m ⁻³)	0.189	0.225	0.491	1.53	0.592	0.489	0.596	0.227	0.644
Dry deposition flux (F_d) ($\mu\text{g m}^{-2} \text{day}^{-1}$)	0.03	0.07	0.23	0.73	0.32	0.30	0.46	0.15	0.54
Aratu#2 PM10									
Geometric mean (ng m ⁻³)	0.110	0.140	0.275	0.901	0.364	0.300	0.439	0.180	0.508
Dry deposition flux (F_d) ($\mu\text{g m}^{-2} \text{day}^{-1}$)	0.02	0.04	0.13	0.43	0.20	0.18	0.34	0.12	0.43
Bananeiras									
Geometric mean (ng m ⁻³)	0.211	0.241	0.432	1.13	0.512	0.473	0.499	0.229	0.529
Dry deposition flux (F_d) ($\mu\text{g m}^{-2} \text{day}^{-1}$)	0.04	0.07	0.20	0.54	0.27	0.29	0.38	0.15	0.44
Lapa									
Geometric mean (ng m ⁻³)	1.15	0.863	2.03	1.01	0.393	0.842	0.559	0.329	0.741
Dry deposition flux (F_d) ($\mu\text{g m}^{-2} \text{day}^{-1}$)	0.20	0.26	0.95	0.48	0.21	0.52	0.43	0.22	0.62

* According to Sheu et al (1996)⁴.

and/or mutagenic than those originating species so are of more concern in health issues). If a PAH is more reactive than other, this is more easily modified (removed) by a photochemical reaction and it would be not found in PM in high level and then dry or wet deposition mechanisms would not be its main atmospheric fate. On the other hand, the less reactive the more probable the PAH is to sink by either dry or wet depositions, depending on its vapour pressure and water solubility (being, therefore, probably promoted to any terrestrial and/or aquatic systems). This should be considered when analyzing some isomer pairs such PHE and ANT, FLT and PYR, BbF and BkF, and IND and DBA. PHE belongs to Class V and ANT is Class II then is reasonable to accept that ANT, being more reactive than PHE, would be more readily modified to any of its possible nitro-derivatives and less ANT would be available to be dry deposited. The same happens with the next two isomer pairs: (i) FLT (Class V) and PYR (Class III), and (ii) IND (Class V) and DBA (Class IV) whose PYR and DBA, respectively, apparently possess lower dry deposition fluxes. In the case of BbF and

BkF pair, both belong to the same reactivity class (Class V) and those high fluxes are derived from both high concentration levels and deposition velocities. Summing up, if dry deposition were the main removal mechanism for PHE, FLT, IND, BbF, BkF and in minor extension, for DBA (and the other Class IV, CRY), those particle airborne once deposited might be resuspended by any mechanical/physical perturbation being then able to be enriched of some PAH freshly generated (vapor-PAH converted to particle or by any physical interaction as accumulation, coagulation, etc acting in both freshly and aged particulate PAH) and be again dry deposited. This cyclic path of those PAH could happen continuously and the particulate matter be aged in relation to some less reactive PAH. The same might happen with NAP, ACY, and tentatively, to ACE and FLU who also are classified as Class V species. But in this case, because they are preferentially segregated to gaseous phase, the main fate of them would be gaseous dry deposition or even wet deposition since they are the most water soluble of the 16 priority PAH.

REFERENCES

1. ALLEN, A ; DA ROCHA, G. O. ; CARDOSO, A ; PATERLINI, W ; MACHADO, C ; DEANDRADE, J . Atmospheric particulate polycyclic aromatic hydrocarbons from road transport in southeast Brazil. Transportation Research. Part D, Transport and Environment, v. 13, p. 483-490, 2008
2. UK Government Expert Panel on Air Quality Standards, available on <http://www.airquality.co.uk/archive/standards.php#std>, accessed February 2008.
3. PEREIRA, P. A. de P.; Lopes, W. A.; Carvalho, L. S.; da Rocha, G. O.; Bahia, N. de C.; Loyola, J.; Quiterio, S. L.; Escaladeira, V.; Arbilla, G.; de Andrade, J. B. Atmospheric concentrations and dry deposition fluxes of particulate trace metals in Salvador, Bahia, Brazil, Atmospheric Environment, 41, 2007, 7837-7850.
4. PEREIRA, P. A. de P.; de Andrade, J. B.; Miguel, A. H. Measurements of semivolatile and particulate polycyclic aromatic hydrocarbons in a bus station and na urban tunnel in Salvador, Brazil, Journal of Environmental Monitoring, 4, 2002, 558-561.
5. LOPES, W A ; DA ROCHA, G. O. ; PEREIRA, P A de P; SANTOS, F. O. ; Carvalho, L. S. ; Bahia, N. de C. ; CONCEICAO, L. S. ; ANDRADE, Jailson B de . Multivariate optimization of a GC-MS method for determination of sixteen priority polycyclic aromatic hydrocarbons in environmental samples. Journal of Separation Science (Online), v. 31, p. 1787-1796, 2008.
6. TASDEMIR, Y.; Esen, F. Dry deposition fluxes and deposition velocities of at an urban site in Turkey. Atmospheric Environment, 41, 2007, 1288-1301.
7. SHEU, H.-L.; Lee, W.-J.; Su, C.-C.; Chao, H.-R.; Fan, Y.-C. Dry deposition of polycyclic aromatic hydrocarbons in ambient air, Journal of Environmental Engineering, 122, 1996, 1101-1109.
8. NIELSEN, T. Reactivity of polycyclic aromatic hydrocarbons toward nitrating species, Environmental Science & Technology, 18, 1984, 157-163.

SPEEDING UP HCl EXTRACTIONS BY EMPLOYING ULTRASOUND ENERGY TO EVALUATE TRACE ELEMENTS BIOAVAILABILITY IN SEDIMENTS**

Vanessa Hatje^a; Leticia M. Costa^b; Maria Graças A. Korn^a and Gabriel Cotrim^a

^aDepartamento de Química Analítica, Universidade Federal da Bahia, Campus de Ondina, 40170-290, Salvador, BA, Brazil

^bDepartamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, MG, Brazil

*e-mail: vhatje@ufba.br

**see more at: HATJE, V., *et al. J. Braz. Chem. Soc.* 2009, 20, 846.

The dissolution of sediment samples is usually necessary for the determination of trace metals using common techniques such as flame and graphite furnace atomic absorption spectroscopy (F AAS, GF AAS), inductively coupled plasma optical emission and mass spectrometry (ICP OES, ICP-MS). The digestion usually requires acid leaching with concentrated mineral acids, with high temperatures and pressure. The wet digestion methods without using HF do not attack the silicate matrix, hence are not considered total digestion. However, for environmental studies, weak leached, such as diluted hydrochloric acid (HCl), is commonly employed to obtain the available and potentially more toxic fraction of metals.

The pre-treatment is usually the most time-consuming step of elemental analysis. Therefore, alternatives have been studied to simplifying and speeding up the conventional methods of sample preparation, for instance, hot plate, microwave and overnight shaking. A number of authors have achieved good results using ultrasound probes and baths (Figure 1a) to reduce time in the pre-treatment of sediments.¹⁻⁴

The ultrasound energy induces acoustic cavitation, which promotes a local high increase in temperature and pressure, allowing high analyte transport from solid particles, eroded and fragmented by the wave shock, to the liquid phase.⁵ The high temperature and pressure also lead to the formation of free radicals and other compounds.⁶⁻⁷ Thus the pre-treatment is usually

shortened compared to conventional methods without the utilization of extreme experimental conditions. The use of ultrasound energy in sample preparation has other advantages, for example does not require special vessels, the ultrasonic cleaning bath is inexpensive and widely available and there is no risk that extraction solution evaporates to dryness as in hot plate digestion.⁶

The aims of this study were: (i) to test the significance of the type of vessel (conical or flat), type of material (Teflon® or glass) and number of replicates, simultaneously prepared, in the ultrasonic bath using three factors analysis of variance; (ii) to speed up conventional extraction using HCl 1.0 mol L⁻¹, largely used in the determination of bioavailable trace metals, by employing ultrasound bath. The tests were carried out using a sediment certified reference material.

A pilot study was performed in order to investigate the influence of type of material (Teflon® or glass), type of vessel bottom (conical or flat) and number of replicates (one or three treated simultaneously) in the efficiency of the extractions of trace elements. Ultrasonic extraction was performed for 30 min, at a previous optimized position in the ultrasonic bath.⁷ A hierarchical sample design was applied, and the results were tested by a three-factor ANOVA. Homogeneity of variances was examined using Cochran's test. Multiple comparisons among means were performed with the Student-Newman-Keul's (SNK) test.

Extractions were conducted on an orbital shaker (Figure 1b) and the supernatants were separated immediately by centrifugation at 3000 rpm for 10 min. The extractions were realized for 0.5 h, 4 h and 12 h at room temperature. For ultrasonic assisted extraction the importance of the length of the sonication process was evaluated. The time range between 60 seconds and 50 minutes. . After sonication, the solution was centrifuged, and the supernatant separated for element determinations by ICP OES. All experiments were performed in triplicates and blanks were also treated as sediment samples.

Results showed that the material of the vessel employed for extractions was significant for Co, Cr, Ni and Mn. The best results were obtained with Teflon[®], with flat bottom. The results also show the viability to work in triplicates in the ultrasonic bath without compromising the efficiency and/or the precision of the extraction.

The recovery percentages for HCl conventional extractions varied from 8.11% (Mn) to 73.4% (Pb and Zn). The low percentages of recovery are not unexpected, since a diluted, cold solution was employed. Nevertheless, most of the results agreed well with data reported by Townsend et al.¹⁵. The extractability power of HCl is clearly dependent on the time of exposure of sediments. Nevertheless, metals reacted differently. Lead, Cu and Zn were rapidly extracted from sediments, indicating a fast kinetic extraction of these labile metals. That is because anthropogenic metals are more likely to be weakly bound to the mineral matrix than elements from lithogenic sources. Slow kinetics reflects

extraction of less mobile, inert phases typical of naturally occurring metals in the sediment matrix.

The results obtained for HCl extraction using ultrasound energy show that for all metals the percentage extracted with ultrasound was below 100% (i.e. certified value concentration). Lead, Zn and Cu were the elements that presented the highest recovery, which is possibly associated to their anthropogenic origin and, therefore, its labile nature. Figure 2 shows a comparison between ultrasonic-assisted leaching rate curves and the results obtained by conventional acid extraction at 0.5, 4 and 12 hours. For the studied elements, leaching efficiency increased with increasing sonication time from 1 to 50 min. For most studied elements the ultrasound-assisted leaching could reduce the conventional extraction time of 12 hours to 50 min (e.g. Cu, Fe e Zn) or even less for Ba (25 min) and Pb (6 min), hence representing and important economy of sample preparation time. Extractions with HCl that employed 4 h exposure time could be performed in less than 50 min of sonication, while sonication time up to 12 min was necessary to reach the extraction efficiency obtained with 0.5 h conventional shaking. For the elements strongly associated to the silicated matrix (i.e. Ni and Cr) the efficiency of sonication was reduced, compared to the more labile elements that presented high concentrations in the sediments.

In conclusion, the ultrasound energy represents a fast, reliable, and safe alternative to conventional acid extraction for the determination of bioavailable metals in sediments, when employing HCl 1.0 mol L⁻¹. The conventional



Figure 1. Ultrasonic bath (A) and orbital shaker (B) used during the experiments.

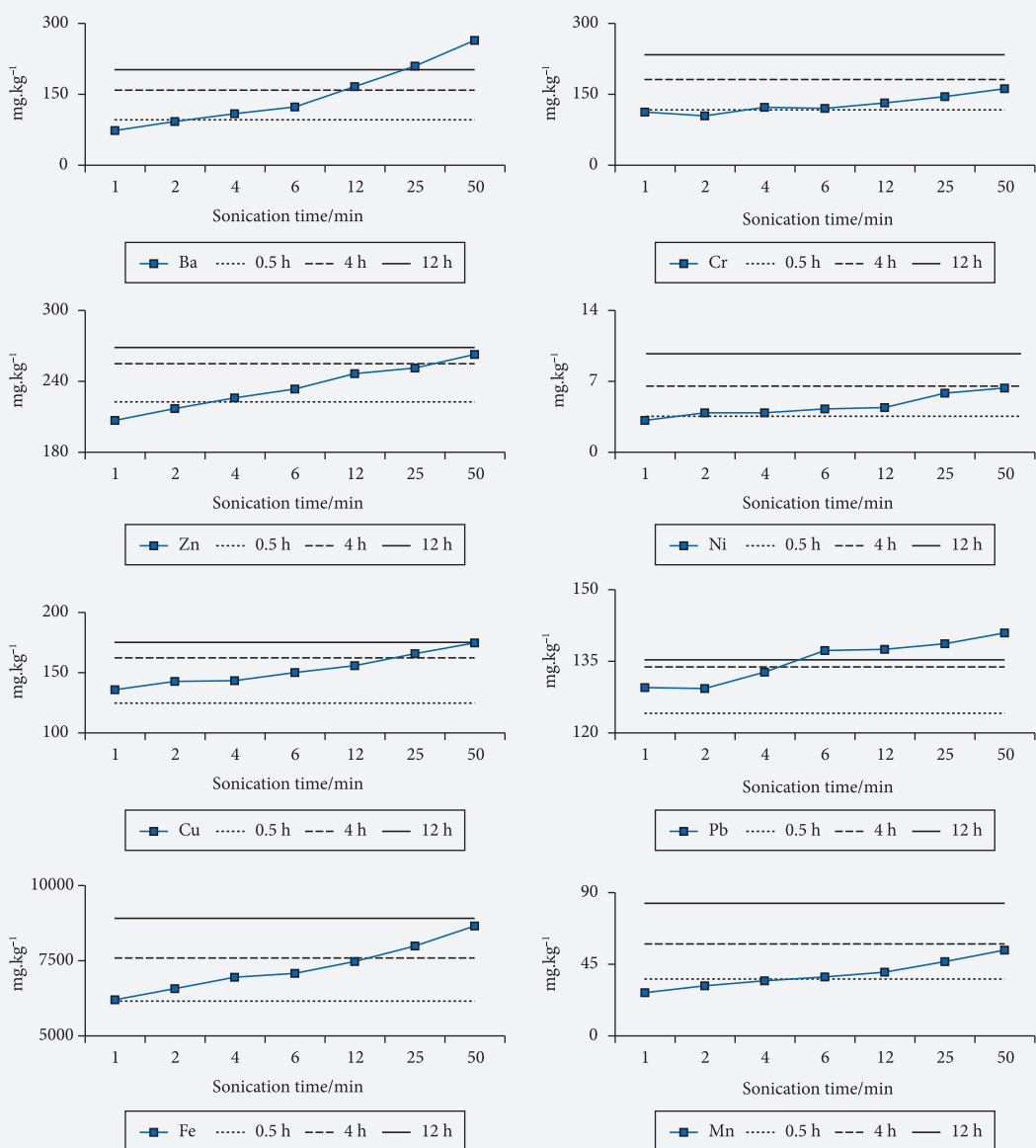


Figure 2. Comparison of extractability from PACS-2 by conventional leaching and ultrasound assisted extraction (line with black squares).

extraction time could be reduced from 12 hours to 6 min, depending on the element of interest and the time used for the conventional extraction. For most elements the precision obtained with ultrasound and conventional extraction was comparable. The study showed that Teflon[®] vessels with flat bottom should be employed, and

triplicate samples could be treated simultaneously in the ultrasonic bath, without compromising the efficiency and/or the precision of the extraction. The ultrasound assisted extraction employing HCl 1.0 mol L⁻¹ is a fast, inexpensive, simple, and reproducible method for the estimation of the availability of trace metals

REFERENCES

1. PEREZ-CID, B., LAVILLA, I., BENDICHO, C., 1998. Speeding up of three-stage sequential extraction method for metal speciation using focused ultrasound *Anal. Chim. Acta* 360, 35-41.
2. BRUNORI, C., IPOLYI, I., MACALUSO, L., 2004. Evaluation of an ultrasonic digestion procedure for total metal determination in sediment reference materials. *Anal. Chim. Acta* 2004, 510, 101-107.
3. Canepari, S.; Cardarelli, E.; Ghighi, S., 2005. Ultrasound and microwave assisted extraction of metals from sediment: a comparison with the BCR procedure. *Talanta* 2005, 66, 1122-1130.
4. GÜNGÖR, H., ELIK, A., 2007. Comparison of ultrasound-assisted leaching with conventional and acid bomb digestion for determination of metals in sediment samples. *Microchem. J.* 2007, 86, 65-70.
5. CAPELO, J.L., GALESIO, M.M., FELISBERTO, G.M., VAZ, C., COSTA PESSOA, J., 2005. Micro-focused ultrasonic solid-liquid extraction (μ FUSLE) combined with HPLC and fluorescence detection for PAHs determination in sediments: optimization and linking with the analytical minimalism concept. *Talanta* 66, 1272-1280.
6. CARVALHO, L.R.F., SOUZA, S.R., MARTINIS, S.B., KORN, M., 1995. Monitoring of the ultrasonic irradiation effect on the extraction of airborne particulate matter by ion chromatography. *Anal. Chim. Acta* 317, 171.
7. NASCENTES, C.C., KORN, M., SOUSA, C.S., ARRUDA, M.A.Z., 2001. Use of ultrasonic baths for analytical applications: a new approach for optimization conditions *J. Braz. Chem. Soc.* 12, 57-63.
8. TOWNSEND, A.T., PALMER, A.S., STARK, S.C., SAMSON, C., SCOULLER, R.C., SNAPE, I., 2007. Trace metal characterisation of marine sediment reference materials MESS-3 and PACS-2 in dilute HCl extracts. *Mar. Pollut. Bull.* 2007, 54, 226-229.

FACTS AND FIGURES



HUMAN RESOURCES

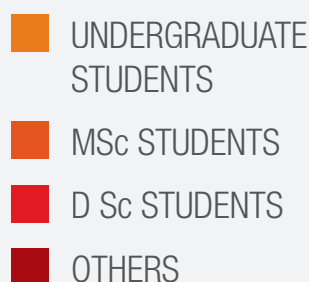
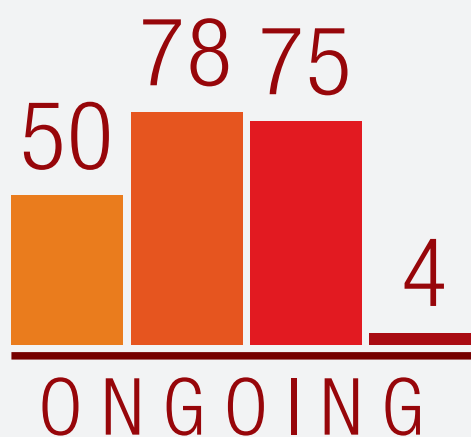
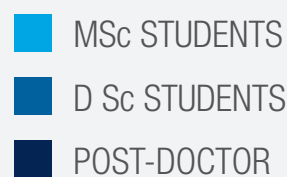
The training of professionals and the formation of highly qualified human resources is part of the strategic goals of the INCT-E&A. To address these emerging challenges, it is necessary to join Science with Education, a fundamental condition to transform the scientific education from the elementary school to the postgraduate formation. In this sense, teachers/researchers are engaged in INCT-EA's tutorial activities and scientific and technological researches, with undergraduate, M Sc and D Sc students. The stage in the postdoctoral level has also been treated as an opportunity for looking to the convergence amongst scientific disciplines and research fields. Also, the scientific/technical stages and visits have been fostered amongst the several research groups which participate in the INCT.

Concerning the INCT activities for training human resources, they can be featured by the number of students of both undergraduate and graduate levels engaged in the projects, as well as the number of D Sc thesis, M Sc dissertations and undergraduate monographs concluded.

It is noteworthy, though, the holding of summer schools with an average of 300 participants in each one, all of them students, teachers and professionals coming from high schools, universities and the industry, from Bahia and other Brazilian states. These Summer Schools have offered several courses in the basic and advanced levels, as well as symposia and conferences conducted by Brazilian and foreign scientists, contributing significantly to the discussion of topics of the INCT's interests and to the training of human resources. Regarding the professionals in industry, there is already a continuous flow of internships and trainings in the INCT laboratories, as well as planned activities during the regular School's semester.

INDICATORS OF EDUCATION HUMAN RESOURCES TRAINING

NUMBERS OF HUMAN RESOURCES IN THE PERIOD



MAIN EVENTS



NATIONAL WEEK OF SCIENCE AND TECHNOLOGY 2009 – SCIENCE IN BRAZIL

Semana Nacional de Ciência e Tecnologia 2009 (SNCT2009) – Ciência No Brasil

The National week of science and Technology (SNCT) event was held in the period of 14 to 19 October 2009 in many cities in Brazil. During this week the INCT-E&A performed two activities in Salvador, Bahia-Brazil.

1. UNDERSTANDING THE POLLUTION IN THE LAPA STATION

The aim of this activity was to inform the public about the air pollutants emitted by vehicle traffic in the Lapa Bus Station (Salvador, Bahia). The Station can have around 460,000 people passing by daily. In 22th October pamphlets, posters and experiments statements setting out the relationship of these emissions with environmental and health problems were installed on a stand at Lapa Station.



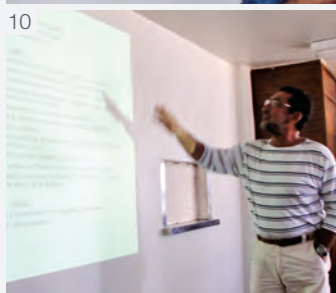
2. THE SCIENTIST RETURNS TO SCHOOL

The goal of this activity was to bring science to young people and scientific activity. In October 23th different activities in the theme were held at the College of Military Police of the Riverside, a public school in Salvador. Students attended the lecture, “Sustainability and the Agenda of the Twenty-first Century”, delivered by Prof. Dr. Jailson B. de Andrade, a professor and coordinator of the INCT-E&A. The students discuss the essence of scientific research, its role in the development of the country and its relationship to education. Moreover, the students had the opportunity to watch demonstrations of experiments in multimedia.



COOPERATION ACTIVITIES BETWEEN INCT GROUPS

INCT-E&A has developed actions seeking to intensify cooperation with other INCT. The most important activity of 2009 was the creation of “I5+”, as a result of the first workshop of cooperation. This event took place in São Lourenço Fort in Itaparica, Bahia, Brazil, with the aim of discussing the governance of the National Institutes on cooperation and strengthening ties in science, technology, and disseminating scientific and teacher training, in from 19 to 21 November 2009. The following are institutes and their coordinators: INCT Complexes and Functional Materials (Coordinator Prof. Galebeck Fernando, UNICAMP), INCT Drugs and Drug (Coordinator Prof. Eliezer Jesus Barreiro, UFRJ), INCT Material Transfer Continent-Ocean (Coordinator Prof. Luiz Drude de Lacerda, UFC), INCT Science and Technology Control of Insect Pests biorational (Coordinator Prof. Fátima Maria das Graças



1 and 2. The São Lourenço Fort (Itaparica, Bahia, Brazil). **3)** Prof. Lidia Moreira; **4)** Prof. Angelo C. Pinto; **5)** Prof. Rosane Marins; **6)** Prof. Vanessa Hatje; **7)** Prof. Eliezer de Jesus Barreiro; **8)** Prof. Luiz Drude de Lacerda; **9)** Profa. Maria Fátima das Graças Fernandes da Silva; **10)** Jailson B. de Andrade.

Fernandes da Silva, UFSCAR) and INCT of Energy and Environment (Coordinator Prof. Jailson Bittencourt de Andrade UFBA).

The workshop was considered very important by participants and should be repeated periodically in the form of a Forum with the participation of others INCTs, encouraging cooperation, convergence and interdisciplinary themes.

42ND IUPAC CONGRESS, 2-7 AUGUST 2009, IN GLASGOW, UK

Symposia: Biofuels co-organised by the Brazilian Chemical Society (SBQ), the Chemical Society of Japan (CSJ) and the RSC

Biodiesel (made from vegetable oil), bioethanol (from carbohydrate fermentation) and conventional fuels synthesised from the gasification products of biomass are key biofuels that need to be exploited to ensure sustainable fuels for the future. The chemical sciences and engineering disciplines are critical in developing efficient catalysts, separation processes, high throughput systems and additives to maximise the effectiveness and efficiency of biofuels. Biofuels have great potential for reducing carbon emissions but it is vitally important that energy used in their production is minimised or derived from renewable resources.

Biofuels may provide fuel with different chemical compositions and this situation is causing a lot of uncertainty both with the fuel producers and suppliers and vehicle manufacturers. There is genuine lack of knowledge of the potential implications of these new fuels becoming widely distributed through a supply chain which has been developed over many decades based on fossil fuels. As with many subjects the ability to characterise bio-fuels, particularly in mixtures with conventional fossil fuels, will be crucial. It is critical therefore that analytical methods and technologies are developed and shared on a global basis.

This symposium was intended to bring together key researchers and innovators active in the area of biomass conversion science to foster international scientific networks and collaborations. The symposium was organized and co-sponsored by the Chemical Societies of Brazil, Japan and the UK - the countries with active research in this important area.

Brazilian researchers in this symposium spoke on the development of research in Brazil.

Among others the following INCT-E&A's researchers were present: Prof. Dr. Jailson B. de Andrade (Coordinator of INCT E&A), Prof. Dr. Claudio J. A. Mota and Prof. Dr. Luiz P. Ramos.



Poster Presentation: **1)** Claudio J. A. Mota; **2)** Jailson B. de Andrade and **3)** Claudio J. A. Mota, Vanderlan Bolzani and Jailson B. de Andrade. **Lecturers:** **4)** Claudio J. A. Mota; **5)** Luiz P. Ramos and **6)** Jailson B. de Andrade

Courses Organized with the INCT FInnancial Support as Part of the of the 15th ENQA - National Meeting on Analytical Chemistry and 3 CIAQA - Iberoamerican Congress on Analytical Chemistry Programming (Salvador - BA, 15 to 10/18/2009)

Flow Techniques and Strategies for Fluid Handling

*Dr. Maria Lúcia Saraiva
(Universidade do Porto, Portugal)*

Especiación Element features: Current Status Future Trends y

*Dr. Yolanda Madrid
(Universidad Complutense, Spain)*

Multidimensional Chromatography

Dr. Elina Bastos Caramão (UFRGS)

Preparation of Samples for Determination of Trace Elements

*Dr. Erico Marlon de Moraes Flores (UFMS)
Dr. Marcia Foster Mesko (UFPel)*

Biosensors

Dr. Lauro Tatsuo Kubota (UNICAMP)

Atomic Absorption Spectrometry High-resolution continuum source (HR-CS AAS)

*Dr. Bernhard Welz (UFSC)
Dr. Maria Goretti R. Vale (UFRGS)*

Multivariate Analysis

*Dr. Maria Fernanda Pimentel (UFPE)
Dr. Wallace Fragoso (UFPB)*

Special Topics in Atmospheric Chemistry

*Dr. Vania Palmeira Campos (UFBA)
Dr. Gisele Olimpio da Rocha (UFBA)*

Courses Organized as Part of Programming the 5th Summer School in Chemistry (Salvador - BA, 22 to 2/25/2010)

Multivariate Analysis (PCA, HCA) in Applied Environmental Assessment Results

Dr. Anderson Santos Souza (UFBA)

Development of Methods in LC-MS-MS - An Approach to Theory and Practice

Mr. Fabio Cremonini Boin (Varian)

Free Radicals and Antioxidants

Dr. André Luis Silva Bacelar Barreiros (UFS)

Panorama and Production of Wines in San Francisco Valley

*Prof. Fabio Lanner Lenk - Winemaker
(Instituto Federal do Sertão Pernambucano)*

Atomic Spectrometry Applied to Environmental Samples

*Dr. Maria das Graças Andrade Korn (UFBA)
Dr. Walter Nei Lopes dos Santos (UNEB)*

QNint: Using New Technologies in the Teaching of Chemistry

*Dr. André Farias de Moura (UFSCar)
Dr. Guilherme Andrade Marson (USP)*

Anthropogenic Impacts in the Coastal Zone

Dr. Vanessa Hatje (UFBA)

Vehicle Emissions and Environmental Impacts

*Dr. Antonio Horacio Miguel
(California Environmental Protection Agency/
Air Resources Board - U.S.)*

Chemical Synthesis: Efficiency and Sustainability

*Dr. Cunha Silvio do Desterro (UFBA),
Dr. Mauricio Moraes Victor (UFBA) and
Dr. Valeria Riatto Belli (UFBA)*

LECTURES AT CONFERENCES, SEMINARS AND CONFERENCES

Symposium: "Acreditação e Materiais de Referência" in 15th ENQA - National Meeting on Analytical Chemistry and 3 CIAQA - Iberoamerican Congress on Analytical Chemistry (Salvador - BA, 15 to 10/18/2009)

*Prof. Maria das Graças A. Korn (IQ/UFBA) and
MSc. Daniel de Castro Lima (IQ, UFBA)*

Coordination of the Section "Chemometrics" in the 15th ENQA - National Meeting on Analytical Chemistry and 3 CIAQA - Iberoamerican Congress on Analytical Chemistry (Salvador - BA, 15 to 18/10/2009)

Prof. Dr. Marcos de Almeida Bezerra - UESB

Coordination Section "Analytical Chemistry Applied to Drug and Drug Abuse" in 15th ENQA - National Meeting on Analytical Chemistry and 3 CIAQA - Iberoamerican Congress on Analytical Chemistry (Salvador - BA, 15 to 10/18/2009)

Prof. Dr. Sivanildo da S. Borges, UFRB

Coordination Section "Analytical Chemistry Applied to Food" at the 15th ENQA - National Meeting on Analytical Chemistry and 3 CIAQA - Iberoamerican Congress on Analytical Chemistry (Salvador - BA, 15 to 10/18/2009)

Prof. Dr. Walter L. Nei dos Santos, UNEB

Lecture "Atomic Absorption Spectrometry for Determination of Metals in Food: Strategies for Increasing Sensitivity" in the 15th ENQA - National Meeting on Analytical Chemistry and 3 CIAQA - Iberoamerican Congress on Analytical Chemistry (Salvador - BA, 15 to 18/10/2009)

Prof. Dr. Valfredo Azevedo Lemos - UESB

Lecture "Mechanization and sequences for calibration and titration" in the 15th ENQA - National Meeting on Analytical Chemistry and 3 CIAQA - Iberoamerican Congress on Analytical Chemistry (Salvador - BA, 15 to 10/18/2009)

Prof. Dr. Mauro Korn - UNEB

Seminar at the Department of Physical Chemistry of the Chemistry Institute of Unicamp. "Chemical Transformation of Glycerol from Biodiesel Production." Campinas.

Prof. Claudio Mota.

Lecture Course on Biodiesel: Collection and Quality Analysis. Chemistry Institute of UFRJ. Rio de Janeiro

Prof. Claudio Mota

- Guest speaker for the Symposium on Biofuels held during the 42nd Congress of the IUPAC. "Biofuels from Glycerine." Glasgow, United Kingdom.

Prof. Claudio Mota

Guest speaker for the 6th Brazilian Conference of Oilseed Plants, Fats and Biodiesel. "Utilization of Glycerol Production of Biodiesel ". Montes Claros.

Prof. Claudio Mota

Lecture at the 8th week in Chemistry at Unicamp. "Chemistry in the Oil Refining, Natural Gas Conversion and Processing of Biomass. Campinas.

Prof. Cláudio Mota

Seminar at the Department of Biochemistry of the IQ-UFRJ. "New Products and Processes from the Glycerine from Biodiesel Production." Rio de Janeiro.

Prof. Claudio Mota

Lecture at the 10th Latin American Conference on Physical Organic Chemistry. "Carbocations on Surfaces: Formation and Stabilization of the Cation Bicyclobutonium on Zeolites." Florianópolis.

Prof. Claudio Mota

Lecture at the third Congress of the Brazilian Biodiesel Technology. "Gliceroquímica". Brasilia.

Prof. Claudio Mota

Seminar at the Department of Chemistry, Technical University of Munich. "New Approaches for Assessing the Acid Strength and carbocation Formation on Zeolites." Munich, Germany.

Prof. Claudio Mota

Lecture at the Symposium Advances and Perspectives of Science in Brazil, Latin America and the Caribbean, organized by the Brazilian Academy of Sciences. "Energy and Environment. Catalysis Conversion of Biomass." Rio de Janeiro.

Prof. Claudio Mota

Guest speaker for the Symposium on Biofuels held during the 42nd Congress of the IUPAC. "Current trends in biodiesel production using heterogeneous catalysts", Glasgow, United Kingdom.

Prof. Luiz P. Ramos.

Guest speaker for the Conference: "R&D Trends on Biofuels in Brazil With the Focus on New Biofuels Technologies" in the German-Brazilian Workshop on Biodiesel and New Biofuels. Berlin, GE, (December 2009).

Prof. Antonio Salvio Mangrich.

PAPERS PRESENTED AT CONFERENCES

JESUS, A. C.; TAMARA S.; COSTA, A. Q.; ZMOZINSKI, A.; SILVA, M. M.; VALE, M. G. R. Determination of biodiesel quality parameters: quantifications of magnesium and calcium using microemulsion by F AAS. In: Colloquium of Analytical Atomic Spectroscopy (CANAS 2009), 2009, Freiberg. Programm Kurzfassungen der Beiträge. , 2009. p.69 – 70.

- DAMIN, I. C. F.; DESSUY, M. B.; CASTILHOS, T. S.; SILVA, M. M.; VALE, M. G. R.; WELZ, B.; KATSKOV, D. A. Comparison of a filter furnace and direct sampling in a platform furnace for lead determination in crude oil samples by GF AAS. In: Tenth Rio Symposium on Atomic Spectrometry, 2008, Salvador. Book of Abstracts. Salvador, 2008. p. 101.
- ZMOZINSKI, A. V.; JESUS, A.; BARBARÁ, J. A.; SILVA, M. M.; VALE, M. G. R. Determinação de Ca, Mg, e Zn em óleo lubrificante por FAAS utilizando solução de três componentes. In: 15º Encontro Nacional de Química Analítica, 2009, Salvador-BA. CD Room do 15º Encontro Nacional de Química Analítica, 2009.
- JESUS, A.; DAMIN, I.C.F.; CASTILHOS, T. S., SCARTAZZINI; R. B.; VALE, M.G.R.; WELZ, B., SILVA, M. M. Determinação direta de arsênio em amostras de petróleo por GF AAS. In: 15º Encontro Nacional de Química Analítica, 2009, Salvador - BA. CD Room do 15º Encontro Nacional de Química Analítica, 2009.
- BECKER, E.; RANPAZZO, R. T.; VALE, M. G. R.; DESSUY, M. B.; SILVA, M. M.; KASTKOV, D.A.; WELZ, BERNHARD. Desenvolvimento de métodos analíticos para a determinação direta de arsênio e chumbo em derivados de petróleo por GF AAS. In: 15º Encontro Nacional de Química Analítica, 2009, Salvador - BA. CD Room do 15º Encontro Nacional de Química Analítica, 2009.
- SILVA, M. M.; JESUS, A.; BARBARÁ, J. A.; ZMOZINSKI, A. V.; GOULART, L. Determinação de sódio, potássio, cálcio e magnésio em biodiesel por espectrometria de absorção atômica utilizando microemulsões In: III Congresso da Rede Brasileira de Tecnologia de Biodiesel, 2009, Brasília-DF. Livro de Resumos do III Congresso da Rede Brasileira de Tecnologia de Biodiesel, 2009. p.181 – 182.
- NUNES, L. S.; BARBOSA, J. T. P.; MOREIRA, F. R. A. M.; RIBEIRO, I.G.C.; KORN, M. G. A.; TEIXEIRA, L. S. G. Determinação de Cu, Fe, Ni e Zn em óleo vegetal por Espectrometria de Absorção Atômica de Alta Resolução com Fonte Contínua. In: 32a Reunião Anual da Sociedade Brasileira de Química, 2009, Fortaleza. Livro de Resumos. São Paulo: SBQ, 2009.
- TEIXEIRA, L. S. G.; BARBOSA, J. T. P.; DOS SANTOS, G. L.; KORN, M. G. A.; KORN, M.; PAIM, A.P.S. Sistema de análise em fluxo para determinação de fosfato por espectrofotometria em fase sólida. In: 32a Reunião Anual da Sociedade Brasileira de Química, 2009, Fortaleza. Livro de Resumos. São Paulo: SBQ, 2009.
- TEIXEIRA, L. S. G.; ASSIS, JÚLIO CÉSAR ROSA; MENDONÇA, D. R.; SANTOS, I.T.V.; GUIMARÃES, P. R. B.; PONTES, L. A. M.; TEIXEIRA, J. S. R. Obtenção de biodiesel de sebo bovino via rota metálica auxiliado por irradiação ultrassônica. In: 32a Reunião Anual da Sociedade Brasileira de Química, 2009, Fortaleza. Livro de Resumos. São Paulo: SBQ, 2009.
- NUNES, L. S.; BARBOSA, J. T. P. ; MOREIRA, F. R. A. M. ; RIBEIRO, I.G.C. ; KORN, MARIA DAS GRAÇAS ANDRADE ; TEIXEIRA, L. S. G. Multi-element determination of Cu, Fe, Ni and Zn content in vegetable oils samples by high-resolution continuum source atomic absorption spectrometry and microemulsion sample preparation. In: 3rd International IUPAC Symposium on Trace Elements in Food, 2009, Roma. Book Abstracts, 2009.
- ALVES, C. T.; BASTOS, L. S.; MACÊDO, L. S.; ANDRADE, H. M. C.; DEMELO, S. A. B. V.; TORRES, E. A. Synthesis and characterization of ZnAl₂O₄ heterogeneous catalyst for biodiesel production. In: 8th World Congress of Chemical Engineering (WCCE8), 2009, Montreal. Proceedings of the 8th World Congress of Chemical Engineering. Ottawa: Canadian Society for Chemical Engineering (CSCHE), 2009. v. 1.
- PERGENTINO, O.; ANDRADE, H. M. C.; MASCARENHAS, A. J. S.. Desidratação de bio-etanol sobre titanoniobatos lamelares pilarizados. 15º Congresso Brasileiro de Catálise & 5º Congresso de Catálise do Mercosul. Armação de Búzios, 2009.
- DE BRITO, M. M.; PERGENTINO, O.; ANDRADE, H. M. C.; MASCARENHAS A. J. S. Síntese hidrotérmica do titanoniobato lamelar (KTiNbO₅) a partir de polioxoniobatos de Lindqvist. 32a Reunião Anual da Sociedade Brasileira de Química, Fortaleza, 2009.
- VICTOR, M. M.; CRUZ, G. S.; DA SILVA, I. M.; CONCEIÇÃO, N. D.; DOS SANTOS, E. L.; ANDRADE, H. M. C.. Uso de Heteropoliácidos do Tipo Keggin na Reação de Esterificação de Ácidos Graxos: uma Alternativa Ambientalmente Correta. 32a Reunião Anual da Sociedade Brasileira de Química, Fortaleza, 2009.
- HATJE, V.; MACEDO, S.M.; DE JESUS, R.M.; COTRIM, G.; SANTANA, F.A.; FERREIRA, L.C. Especificação de As em sedimentos estuarinos da Baía de Todos os Santos, BA. In: 15 ENQA, 2009, Salvador. In: CD de resumos.

- MACEDO, S. M.; DE JESUS, R. M.; HATJE, V.; FERREIRA, S.L.C. Especificação de As inorgânico em fertilizante a base de superfosfato, rochas fosfatadas e sedimentos em pregando amostragem de suspensão e HG FAAS. In: Congresso Uruguayo de Química Analítica, 2009, Montevideo. Livro de Resumos do I Congresso Uruguayo de Química Analítica, 2009.
- HATJE, V.; MACEDO, S.M.; DE JESUS, R.M.; COTRIM, G.; SANTANA, F.A.; FERREIRA, S.L.C. Asspeciation in estuarine sediments of Todos os Santos Bay, BA, Brasil. In: XIII Congresso Latinoamericano de Ciências del Mar, 2009, Havana. Cd do Anais do XIII Congresso Latinoamericano de Ciências del Mar, 2009.
- HATJE, V.; SOUZA, M.C.M.B.; CARICCHIO, C. Avaliação preliminar de risco a saúde humana devido ao consumo de invertebrados marinhos. In: XIII COLACMAR, 2009, Havana. CD do Anais do XIII ColacMarCuba, 2009.
- COTRIM, G.; BARROS, F.; HATJE, V. Avaliação da biodisponibilidade de metais traço em sedimentos estuarinos. In: XIII ColacMarCuba, 2009, Havana. Cd do Anais do XIII ColacMarCuba, 2009.
- GUARIEIRO, A. L. N.; DA ROCHA, G. O.; CONCEICAO, L. S.; LOPES, W. A.; PEREIRA, PEDRO A DE P.; ANDRADE, JAILSON B. DE. Evaluation of airborne polycyclic aromatic hydrocarbons from Itaparica Island, Bahia, Brazil. In: European Aerosol Conference 2009, 2009, Karlsruhe, Alemanha. European Aerosol Conference 2009. European Aerosol Conference 20 : European Aerosol Conference 2009, 2009. v. unico. p. 1-2.
- GUARIEIRO, A. L. N.; DA ROCHA, G. O.; CARDOSO, M.; ANDRADE, J. B. DE. Desenvolvimento de metodologia analítica para determinação de Nitro-HPA em material particulado atmosférico por GC-MS. In: 15o Encontro Nacional em Química Analítica, 2009, Salvador-BA. 15o Encontro Nacional em Química Analítica. Salvador : SBQ, 2009. v. unico. p. 1-2.
- ANUNCIAÇÃO, D. S.; SOUSA, E. T.; CARVALHO, A. B. DE.; PEREIRA, P. A. DE P.; ANDRADE, J. B. DE. Perfis de emissão de compostos carbonílicos (CC) em fase gasosa durante a produção de carvão vegetal em uma carvoaria da Bahia. In: 32 Reunião Anual da Sociedade Brasileira de Química, 2009, Fortaleza. CD de resumos, 2009.
- BASTOS, L. C. S.; PEREIRA, P. A. P. Estudo da influência de íons metálicos nas taxas de emissão de compostos carbonílicos por óleo de canola submetido a aquecimento contínuo à temperatura de 180 C. In: 32 Reunião Anual da Sociedade Brasileira de Química, 2009, Fortaleza. CD de resumos, 2009.
- GUARIEIRO, A. L. N.; DA ROCHA, G. O.; CONCEIÇÃO, L. S.; LOPES, W. A.; PEREIRA, P. A. P.; DE ANDRADE, J. B. Avaliação de HPAs de Aesossóis Atmosféricos da Ilha De Itaparica Ba. In: 32 Reunião Anual da Sociedade Brasileira de Química, 2009, Fortaleza. CD de resumos, 2009.
- DA ROCHA, G. O.; OTUBO, L.; ALVES, O. L.; PEREIRA, P. A. P.; DE ANDRADE, J. B. Morfologia de Nanopartículas Atmosféricas por Microscopia Eletrônica De Varredura (SEM). In: 32 Reunião Anual da Sociedade Brasileira de Química, 2009, Fortaleza. CD de resumos, 2009.
- MENEZES FILHO, A.; SANTOS, F. N.; PEREIRA, P. A. P. Desenvolvimento, validação e aplicação de metodologia analítica para determinação de resíduos de pesticidas em manga por SPME-GC-MS. In: 32 Reunião Anual da Sociedade Brasileira de Química, 2009, Fortaleza. CD de resumos, 2009.
- TAVARES, J. T. Q.; MENEZES FILHO, A.; PEREIRA, P. A. DE P. Análise de COV por HS-SPME e GC-MS em fermentado de cana natural e pasteurizado, envelhecidos em garrafas e barris de carvalho. In: 32 Reunião Anual da Sociedade Brasileira de Química, 2009, Fortaleza. CD de resumos, 2009.
- SMICHOVSKI, P.; ANDRADE, M. F.; BEHRENTZ, E.; ZACARIAS, D.; NASCIMENTO, K.; CAVALCANTE, F.; VASCONCELLOS, P. C. Determinación de Metales, Metaloides, Iones, Compuestos Orgánicos y Negro de Carbón en Material Particulado Colectado en Tres Ciudades de América Latina. In: II Congreso Colombiano ey Conferencia Internacional de Calidad del Aire, 2009, Cartagena - Colômbia. II Congreso Colombiano ey Conferencia Internacional de Calidad del Aire, 2009.

↙ PUBLICATION



PAPERS

- ALLEN, A.G., MCGONIGLE, A.J.S., CARDOSO, A.A., MACHADO, C.M.D, DAVISON, B., PATERLINI, W.C., ROCHA, G.O., ANDRADE, J.B., 2009. Influence of sources and meteorology on surface concentrations of gases and aerosols in a coastal industrial complex. *Journal of the Brazilian Chemical Society* 20, 2214-2221.
- ALMEIDA, B.L., VERSIANI, O., SOUSA, M., MERCÊ, A.L.R., MANGRICH, A.S., FELCMAN, J., 2009. Synthesis and characterization of new ternary Cu(II)-polyamines-ATP complexes. *Inorganica Chimica Acta* 362, 2447-2451.
- ARAUJO, R.G.O., WELZ, B., VIGNOLA, F., BECKER-ROSS, H., 2009. Correction of structured molecular background by means of high-resolution continuum source electrothermal atomic absorption spectrometry. Determination of antimony in sediment reference materials using direct solid sampling. *Talanta* 80, 846-852.
- BALIZA, P.X., TEIXEIRA, L.S.G., LEMOS, V.A., 2009. A procedure for determination of cobalt in water samples after dispersive liquid-liquid microextraction. *Microchemical Journal* 93, 220-224.
- BATISTA, B.L., RODRIGUES, J.L., TORMEN, L., CURTIUS, A.J., BARBOSA JR, F., 2009. Reference concentrations for trace elements in urine for the Brazilian population based on q-ICP-MS with a simple dilute-and-shoot procedure. *Journal of the Brazilian Chemical Society* 20, 1406-1413.
- BORGES, D.L.G., STURGEON, R.E., WELZ, B., CURTIUS, A.J., MESTER, Z., 2009. Ambient mass spectrometric detection of organometallic compounds using direct analysis in real time. *Analytical Chemistry* 81, 9834-9839.
- CUNHA, S.D., DA SILVA, T.L., 2009. One-pot and Catalyst-Free Synthesis of Thiosemicarbazones via Multicomponent Coupling Reactions. *Tetrahedron Letters* 50, 2090-2093.
- DA CUNHA, M.E., KRAUSE, L.C., MORAES, M.S.A., FACCINI, C.S., JACQUES, R.A., ALMEIDA, S.R., RODRIGUES, M.A. CARAMÃO, E.B. 2009. Beef tallow biodiesel produced in a pilot scale. *Fuel Processing Technology* 90, 570-575.
- DAMIN, I.C.F., DESSUY, M.B., CASTILHOS, T.S., SILVA, M.M., VALE, M. G. R. ; WELZ, B.; KATSKOV, D. A., 2009. Comparison of direct sampling and emulsion analysis using a filter furnace for the determination of lead in crude oil by graphite furnace atomic absorption spectrometry? *Spectrochimica Acta. Part B, Atomic Spectroscopy* 64, 530-536.
- DA ROCHA G.O., LOPES, W.A., PEREIRA, P.A.P., VASCONCELLOS, P.D., OLIVEIRA, F.S., CARVALHO, L.S., CONCEIÇÃO, L.D.S., DE ANDRADE, J.B., 2009. Quantification and Source Identification of Atmospheric Particulate Polycyclic Aromatic Hydrocarbons and their Dry Deposition Fluxes at Three Sites in Salvador Basin, Brazil, Impacted by Mobile and Stationary Sources. *Journal of the Brazilian Chemical Society* 20, 680-692.
- DA SILVA, C.R.B., GONÇALVES, V.L.C., LACHTER, E.R., MOTA, C.J.A., 2009. Etherification of Glycerol with Benzyl Alcohol Catalyzed by Solid Acids. *Journal . Brazilian. Chemical. Society* 20, 201-204.
- DA SILVA, C.X.A.; GONÇALVES, V.L.C.; MOTA, C.J.A., 2009. Water-Tolerant Zeolite Catalyst for the Acetalisation of Glycerol. *Green Chemistry* 11, 38-41.
- DITTERT, I.M., SILVA, J.S.A., Araujo, R.G.O., CURTIUS, A. J., WELZ, B., BECKER-ROSS, H., 2009. Direct and simultaneous determination of Cr and Fe in crude oil using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Spectrochimica Acta. Part B, Atomic Spectroscopy* 64, 537-543.
- DITTERT, I.M., BORGES, D.L.G., WELZ, B., CURTIUS, A.J., BECKER-ROSS, H., 2009. Determination of silver in geological samples using high-resolution continuum source electrothermal atomic absorption spectrometry and direct solid sampling. *Microchimica Acta* 167, 21-26.
- DOS SANTOS, L.M.G., WELZ, B., ARAUJO, R.G.O., JACOB, S.D., VALE, M.G.R., MARTENS, A., MARTENS, I.B.G., BECKER-ROSS, H., 2009. Simultaneous Determination of Cd and Fe in Beans and Soil of Different Regions of Brazil Using High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry and Direct Solid Sampling. *Journal of Agricultural and Food Chemistry* 57, 10089-10094.
- FERNANDES, D.R., ROSENBAACH JR., N., MOTA, C.J.A., 2009. Catalytic conversion of chloromethane to methanol and dimethyl ether over metal-exchanged zeolite Y. *Applied Catalysis A: General* 367, 108-112.
- FERNÁNDEZ, T.L., SOUZA, E.T., VISENTIN, L.C., SANTOS, J.V., MANGRICH, A.S., FARIA, R.B., ANTUNES, O.A.C., SCARPELLINI, M., 2009. A new oxo-vanadium complex employing an imidazole-rich tripodal ligand: A bioinspired bromide and hydrocarbon oxidation catalyst. *Journal of Inorganic Biochemistry* 103, 474-479.
- FERREIRA, S.L.C., DE JESUS, R.M., MATOS, G.D., DE ANDRADE, J.B., BRUNS, R.E., DOS SANTOS, W.N.L., CAVALCANTE, D.D., VALE, M.G.R., DESSUY, M.B., 2009. Multivariate optimization and validation of an analytical method for the determination of cadmium in wines employing ETASS. *Journal of the Brazilian Chemical Society* 20, 788-794.

- GUARIEIRO, L.L.N., DE SOUZA, A.F., TORRES, E.A., DE ANDRADE J.B., 2009. Emission profile of 18 carbonyl compounds, CO, CO₂, and NO_x emitted by a diesel engine fuelled with diesel and ternary blends containing diesel, ethanol and biodiesel or vegetable oils. *Atmospheric Environment* 43, 2754–2761.
- GUIMARÃES, T.B.F., PEPE, I.F.S., MANGRICH, A.S., DE ANDRADE, J.B., SILVA, L.A., 2009. Optical properties of colloids formed in copper tin sulfate solution containing Rhodamine B. *Journal of Alloys and Compounds* 481(1-2), 654-658.
- HATJE, V., COSTA, L.M., KORN, M.G.A., COTRIM, G., 2009. Speeding up HCl extractions by employing ultrasound energy to evaluate trace elements bioavailability in sediments. *Journal of the Brazilian Chemical Society* 20, 846-852.
- MACHADO, K.D., SANCHEZ, D.F., MACIEL, G.A., BRUNATTO, S.F., MANGRICH, A.S., STOLF, S.F., 2009. Vibrational, optical and structural studies of an amorphous Se S alloy produced by mechanical alloying. *Journal of Physics: Condensed Matter* 21, 195406 (9pp).
- MACHADO, M.C.S., LOYOLA, J., QUITERIO, S.L., DA ROCHA, G.O., DE ANDRADE, J.B., ARBILLA, G., 2009. Particle-associated polycyclic aromatic hydrocarbons and their dry deposition fluxes from a bus-station in the Rio de Janeiro metropolitan area, Brazil. *Journal of the Brazilian Chemical Society* 20, 1565-1573.
- MANGRICH, A.S., DA SILVA, L., PEREIRA, B.F., MESSERSCHMIDT, I., 2009. Proposal of an EPR based method for pollution level monitoring in mangrove sediments. *Journal of the Brazilian Chemical Society* 20, 294-298, 2009.
- MARQUES, C.A.X., FONTES, C.H., EMBIRUÇU, M., KALID, R.A., 2009. Efficiency control in a commercial counter flow wet cooling tower. *Energy Conversion and Management* 50, 2843-2855.
- MOTA, C.J.A., da SILVA, C.X.A., GONÇALVES, V.L.C., 2009. Gliceroquímica: Novos Produtos e Processos a partir da Glicerina de Produção de Biodiesel. *Química Nova* 32, 639-649.
- NARDI, E., EVANGELISTA, F., TORMEN, L., SAINTPIERRE, T.D., CURTIUS, A.J., SOUZA, S., BARBOSA JR, F., 2009. The use of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of toxic and essential elements in different types of food samples. *Food Chemistry* 112, 727-732.
- NEVES, A.P., BARBOSA, C.C., GRECO, S.J., VARGAS, M.D., VISENTIN, L.C., PINHEIRO, C.B., MANGRICH, A.S., BARBOSA, J.P., DA COSTA, G.L. 2009. Novel Aminonaphthoquinone Mannich Bases Derived from Lawsone and their Copper(II) Complexes: Synthesis, Characterization and Antibacterial Activity. *Journal of the Brazilian Chemical Society* 20, 712-727.
- NICOLINI K.P., FUKAMACHI, C.R.B., WYPYCH, F., MANGRICH, A.S., 2009. Dehydrated halloysite intercalated mechanochemically with urea: Thermal behavior and structural aspects. *Journal of Colloid and Interface Science*, 474 - 479, 2009.
- NICOLINI, K.P., LOMBARDI, K.C., SCHREINER, W.H., MAZZARO, I., WYPYCH, F., MANGRICH, A.S., 2009. Evidence of weathering stages of phyllosilicates from biotite/muscovite to kaolinite, probed by EPR spectroscopy. *Mineralogy and Petrology* 97, 139–144.
- NOVOTNY, E.H., HAYES, M.H.B., MADARI, B.E., BONAGAMBA, T.J., DE AZEVEDO, E.R., DE SOUZA, A.A., SONG, G., NOGUEIRA, C.M., MANGRICH, A.S., 2009. Lessons from the Terra Preta de Índios of the Amazon region for the utilisation of charcoal for soil amendment. *Journal of the Brazilian Chemical Society* 20, 1003-1010, 2009.
- OLENDZKI, R.N., IGNÁCIO, A.C., MANGRICH, A.S., 2009. Uso da técnica de luminescência total na investigação dos efeitos de diferentes manejos do solo para arroz sobre as substâncias húmicas de um planossolo. *Revista Brasileira de Ciência do Solo*. 33, 1147 - 1152, 2009.
- PINHEIRO, A.S., DE ANDRADE, J.B., 2009. Development, validation and application of a SDME/GC-FID methodology for the multiresidue determination of organophosphate and pyrethroid pesticides in water. *Talanta* 79, 1354-1359.
- QUINTELLA, C.M., TEIXEIRA, L.S.G., KORN, M.G.A., NETO, P.R.C., TORRES, E.A., CASTRO, M., JESUS, C.A.C., 2009. Cadeia do biodiesel da bancada a indústria: uma visão com prospecção de tarefas e oportunidades para P&D&I, *Química Nova* 32, 793-808.
- SANTOS, W.P.C., CASTRO, J.T., BEZERRA, M.A., FERNANDES, A.P., FERREIRA, S.L.C., KORN, M.G.A. Application of multivariate optimization in the development of an ultrasound-assisted extraction procedure for multielemental determination in bean seeds samples using ICP OES. *Microchemical Journal* 91, 153-158, 2009.
- SANTOS, E.J., HERRMANN, A.B., DECAIRES, S., FRESCURA, V.L.A., CURTIUS, A.J., 2009. Determination of Se in biological samples by axial view inductively coupled plasma optical emission spectrometry after digestion with aqua regia and on-line chemical vapor generation. *Spectrochimica Acta Part B, Atomic Spectroscopy* 64, 549-553.
- SOUZA, E. T., DE OLIVEIRA, F.S., CARDOSO, A.A., ANDRADE, J.B., 2009. A semi-continuous analyzer for the fluorimetric determination of atmospheric formaldehyde. *Journal of the Brazilian Chemical Society* 20, 259-265.
- SOLDI, R.A., OLIVEIRA, A.R.S., RAMOS, L.P., CÉSAR-OLIVEIRA, M.A.F., 2009. Soybean oil and beef tallow alcoholysis by acid heterogeneous catalysis. *Applied Catalysis. A, General* 361, 42-48.

- TEIXEIRA, L.S.G., ASSIS, J.C.R., MENDONÇA, D.R., SANTOS, I.T.V., GUIMARÃES, P.R.B., PONTES, L.A.M., TEIXEIRA, J.S.R., 2009. Comparison between conventional and ultrasonic preparation of beef tallow biodiesel. *Fuel Processing Technology*, 1164-1166.
- TEIXEIRA, L.S.G., CHAVES, T.J., GUIMARÃES, P.R.B., PONTES, L.A.M., TEIXEIRA, J.S.R., 2009. Indirect determination of chloride and sulfate ions in ethanol fuel by X-ray fluorescence after a precipitation procedure. *Analytica Chimica Acta*, p. 29-32.
- TORRES, D.P., BORGES, D.L.G., FRESCURA, V.L.A., CURTIUS, A.J., 2009. A simple and fast approach for the determination of inorganic and total mercury in aqueous slurry of biological samples using cold vapor atomic absorption spectrometry and in situ oxidation. *Journal of Analytical Atomic Spectrometry* 24, 1118-1122.
- TORRES, D.P., FRESCURA, V.L.A., CURTIUS, A.J., 2009. Simple mercury fractionation in biological samples by CV AAS following microwave-assisted acid digestion or TMAH pre-treatment. *Microchemical Journal* 93, 206-210.
- VELOSO, M.C.C., OLIVEIRA, A.S., DE ANDRADE, J.B., SILVA, V.M., SANTOS, G.V., 2009. Bromophenol concentrations in fish from Salvador, BA, Brazil. *Anais da Academia Brasileira de Ciências* 81, 165-172.

BOOK

- HATJE, V.; DE ANDRADE J.B. *Baía de Todos os Santos: aspectos oceanográficos*. 1. ed. Salvador: EDUFBA, 2009. v. 1. 306 p.

BOOK CHAPTERS

- DE ANDRADE J.B.; HESSA, P.; JOHNSTONB, M.; BROWN-STEINERA, B.; HOLLOWAYB, T. Air Quality Issues Associated with Biofuel Production and Use.. In: Peter Hessa, Matt Johnstonb, Benjamin Brown-Steinera, Tracey Hollowayb, Jailson B. de. (Org.). *Biofuels : Environmental Consequences & Implications of Changing Land Use*, 2009, v. 10, p. 169-194.
- HATJE, V.; BÍCEGO, M.; CORREIA, G.; DE ANDRADE, J. B. Contaminação Química. In: Vanessa Hatje; Jailson B. de Andrade. (Org.). *Baía de Todos os Santos: aspectos oceanográficos*. Salvador: EDUFBA, 2009, v. 1, p. 243-298.
- HATJE, V.; DE ANDRADE, J.B. Introdução. In: Vanessa Hatje; Jailson B. de Andrade. (Org.). *Baía de Todos os Santos: aspectos oceanográficos*. Salvador: EDUFBA, 2009, v. 1, p. 15-24.

PATENTS

- QUINTELLA, C. M., GUIMARÃES, A. K, MUSSE, Ana Paula Santana, PATENTE tipo PI Nacional em fase de sigilo - MÉTODO PARA MONITORAR QUALIDADE EM PROCESSOS DE OBTENÇÃO DE COMBUSTÍVEIS E DISPOSITIVO SENSOR PARA SUA OPERAÇÃO, 2009.
- TORRES, E.A., GUARIEIRO, L.L.N., PEREIRA, P.A.P., de ANDRADE, J.B. PATENTE tipo PI Nacional em fase de sigilo - TÚNEL DE DILUIÇÃO PARA AMOSTRAGEM A VOLUME CONSTANTE DE GASES E MATERIAL PARTICULADO EMITIDOS NA EXAUSTÃO DE MOTORES VEICULARES, 2009.
- RIBEIRO, N.; MACHADO, A.; DE ANDRADE J.B. MÉTODO DE QUANTIFICAÇÃO DE GLICERINA, ORIUNDA DO PROCESSO DE OBTENÇÃO DO BIODIESEL, POR CROMATOGRAFIA EM FASE GASOSA, 2009.



Baía de Todos os Santos - Aspectos Oceanográficos cover's book.



Biofuels: Environmental Consequences & Implications of Changing Land Use cover's book and a view of the paper "Air Quality Issues Associated with Biofuel Production and Use."

TODOS OS SANTOS BAY: A MULTI AND TRANSDISCIPLINARY STUDY

Coordination: *Dr. Jailson B. De Andrade (UFBA)*

Vice-coordination: *Vanessa Hatje (UFBA) and Núbia M. Ribeiro (IFBA)*

FAPESB Conv. 049/2008 (R\$ 1869304.00; 2008-2012)

Todos os Santos Bay (BTS) is centered at 12°50'S latitude and 38°38'W (Figure 1) longitude, and possesses a maximum width and length of 32 km and 50 km, respectively. BTS is located in the vicinity of Salvador, the third largest metropolitan area of Brazil, and the home of the largest petrochemical complex in the southern hemisphere. Several anthropogenic activities influence the system's environmental quality, such as the influx of domestic effluents, solid wastes, agriculture, industrial (chemicals, petrochemicals, smelters, etc.) and mining activities (CRA, 2008; Hatje and de Andrade, 2009; Hatje et al., 2010). As a result, relatively high concentrations of trace elements and hydrocarbons (HPAs) are observed in marine invertebrates (Wallner-Kersanach et al., 2000; CRA, 2004; Amado Filho et al., 2008; Santil et al., 2010; Hatje et al., 2009), sediments (CRA, 2004; Venturini et al., 2004; Hatje et al., 2006,

Barros et al., 2008; Venturini et al; 2008; Hatje et al., 2009; Hatje et al., 2010), and atmospheric particles (Pereira et al., 2007; da Rocha et al., 2009), especially in the northern region.

The Paraguaçu, Subaé and Jaguaripe River (Figure 1) are the three main tributaries of the BTS. The catchment of the Paraguaçu River is 56,300 km², and downstream of the Pedra do Cavalo Dam, Paraguaçu presents an average discharge of 64 m³ s⁻¹ (Genz, 2006). Maximum flows are observed in summer months, especially in December and January. The other two main catchments of the BTS are the Jaguaripe (2,200 km²) and Subaé River (600 km²). The maximum discharge of the Jaguaripe and Subaé River occurs in June (winter), where a mean monthly discharge of 28 m³s⁻¹ and 9 m³s⁻¹ is observed, respectively (Cirano and Lessa, 2007). Despite the social, economic and artistic importance of the region, there are only a

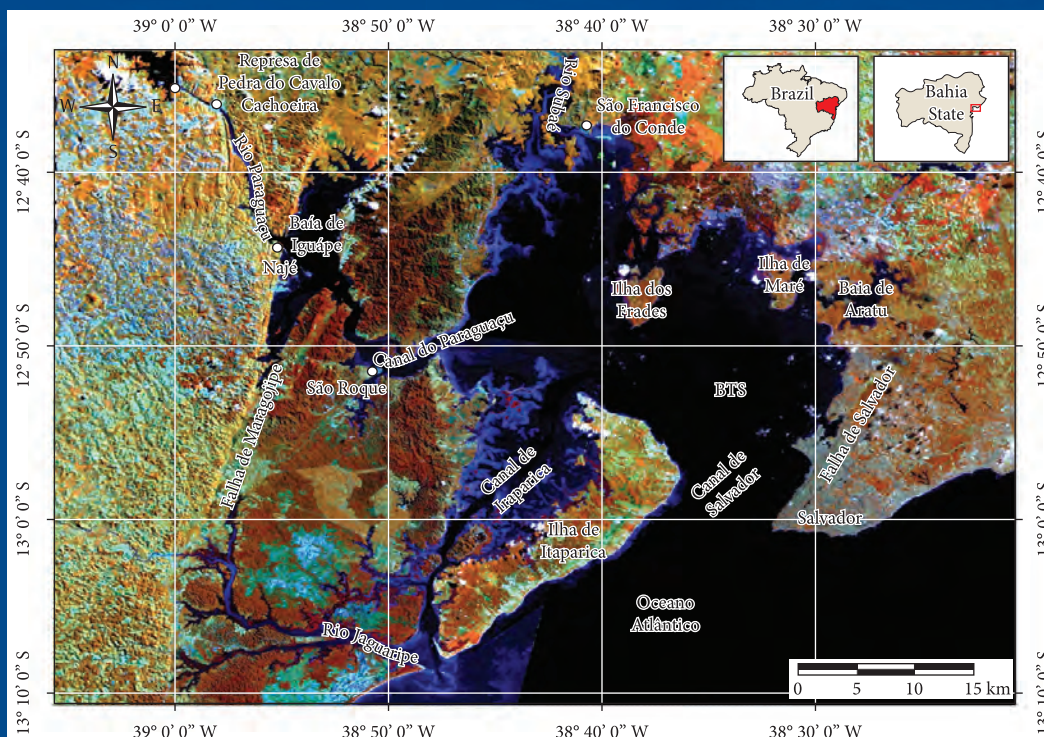


Figure 1. Todos os Santos Bay, Bahia, Brazil.



limited number of publications in the international literature. The number of studies is small, not only regarding the oceanographic aspects of the bay, and the fluxes of organic and inorganic contaminants at the interfaces continent-ocean-atmosphere, but also about the biodiversity, the potential use of biota as environmental biomarkers and/or its pharmaceutical and biotechnological applications. Not to mention the artistic potentiabilities of the people and the region itself, which are unlimited in the most diverse areas, including music, traditional dances, religious and cultural manifestations.

The main objective of this project is to study Todos os Santos Bay, in a multi and transdisciplinary way, constructing a long term database of the oceanography, biodiversity, human sciences and arts, practiced in the area, in order to contribute to the sustainable management of the BTS, especially, concerning the environmental and human quality of life.

This project is based on the articulation of four main research groups: Education, Arts, Oceanography and Natural Resources and Biodiversity. Groups share laboratory facilities and field work gear/instruments, work under the same sampling/preservation protocols, and synchronize field work activities to favors spatial and temporal

data compatibility, as well as, economy through the project. Six workshops already occurred, to discuss the management of the project, research articulations and presentation of the partial results. Data generated during the projects and these workshops are used to compose a long term database to be available at Instituto Kirimuré (www.btsinstitutokirimure.ufba.br).

It is expected that this Project generates a solid knowledge about the spatial and temporal distribution of fauna, flora, and contaminants, as well as, fluxes between interfaces of Todos os Santos Bay. The results are to be published in conferences, international journals and at the webpage www.btsinstitutokirimure.ufba.br. The participation of students from several areas, such as biology, chemistry, oceanography, arts, etc, at all levels (undergrad, graduated, postdoctoral and technical courses), is an innovation of this study and it is strongly supported by the project. Moreover the knowledge generated will provide a substantial amount of information to support the work of environmental agencies and decision makers in the management and preservation of the area and its population.

For references see www.institutokirimure.ufba.br



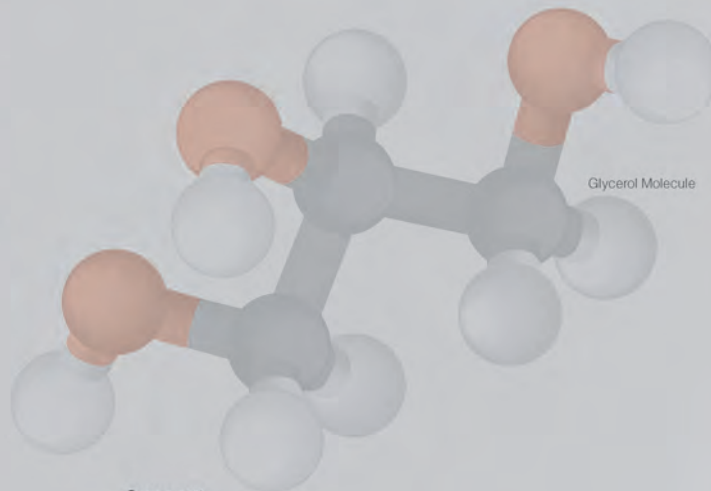
ENERGIA & AMBIENTE

**National Institute of
Science and Technology for
Energy & Environment**

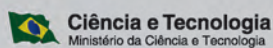
Headquarters Universidade Federal da Bahia
Centro Interdisciplinar de Energia e Ambiente
Rua Barão de Jeremoabo, S/N - Ondina
CEP: 40170115Salvador – Bahia

Telephone +55 71 3283 6821

Home Page www.inct.cienam.ufba.br



Support



Collaborations



Marinha do Brasil



FAFEN

