SCIENCO

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

ISSN 0104-5431

AN INTERNATIONAL FORUM FOR THE RAPID PUBLICATION
OF ORIGINAL SCIENTIFIC ARTICLES DEALING WITH CHEMISTRY AND
RELATED INTERDISCIPLINARY AREAS

VOLUME SIX, NUMBER SIX

JULY 1998

EDITOR

LAVINEL G. IONESCU, Departamento de Química, CCNE, Universidade Luterana do Brasil, Canoas, RS & Instituto de Química, Pontifícia Universidade Católica do Rio Grande do Sul, Porto Alegre, RS BRASIL

EDITORIAL BOARD

D. BALASUBRAMANIAN, Centre for Cellular and Molecular Biology, Hyderabad, INDIA
HÉCTOR E. BERTORELLO, Departamento de Quimica Organica, Facultad de Ciencias Quimicas, Universidad Nacional de Cordoba, Cordoba, ARGENTINA
AÉCIO P. CHAGAS, Instituto de Química, UNICAMP, Campinas, SP, BRASIL
JUAN JOSÉ COSA, Departamento de Quimica y Fisica, Facultad de Ciencias Exactas, Universidad Nacional de Rio Cuarto, Rio Cuarto, ARGENTINA
GLENN A. CROSBY, Department of Chemistry, Washington State University, Pullman, WA, USA
VITTORIO DEGIORGIO, Dipartimento di Elettronica, Sezione di Fisica Applicata, Università di Pavia, Pavia, ITALIA
JOSÉ C. TEIXEIRA DIAS, Departamento de Química, Universidade de Coimbra, Coimbra, PORTUGAL
XORGE A. DOMINGUEZ, Departamento de Quimica, Instituto Tecnologico y de Estudios Superiores de Monterrey, Monterrey, N.L., MÉXICO
OMAR A. EL SEOUD, Instituto de Química, Universidade de São Paulo São Paulo, SP, BRASIL

ERNESTO GIESBRECHT, Instituto de Química, Universidade de São Paulo, São Paulo, SP, BRASIL
FERNANDO GALEMBECK, Instituto de Química, UNICAMP, Campinas, SP, BRASIL

NISSIM GARTI, Casali Institute of Applied Science, Hebrew University of Jerusalem, Jerusalem, ISRAEL
GASPAR GONZALEZ, Centro de Pesquisa, CENPES-PETROBRAS, Ilha do Fundão, Rio de Janeiro, RJ, BRASIL
YOSHITAKA GUSHIKEM, Instituto de Química, UNICAMP, Campinas, SP, BRASIL
WILLIAM HASE, Department of Chemistry, Wayne State University, Detroit, MI, USA
I. B. IVANOV, Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, Sofia, BULGARIA
IVAN IZQUIERDO, Departamento de Bioquímica, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, BRASIL

V.A. KAMINSKY, Karpov Institute of Physical Chemistry, Moscow, RUSSIA

MICHAEL LAING, Department of Chemistry, University of Natal, Durban, SOUTH AFRICA
EDUARDO LISSI, Departamento de Quimica, Universidad de Santiago de Chile, Santiago, CHILE
WALTER LWOWSKI, Department of Chemistry, New Mexico State University, Las Cruces, N.M., USA
C. MANOHAR,Bhabha Atomic Research Centre, Chemistry Division, Bombay, INDIA
AYRTON FIGUEIREDO MARTINS, Departamento de Química,Universidade Federal de Santa Maria, Santa Maria, RS, BRASIL
FRED MENGER, Department of Chemistry, Emory University, Atlanta, GA, USA
MICHAEL J. MINCH, Department of Chemistry, University of the Pacific, Stockton, CA, USA
K. L. MITTAL, IBM Corporate Technical Institutes, Thornwood, N.Y., USA
ARNO MULLER, Escola de Engeharia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, BRASIL

JOSE MIGUEL PARERA, Instituto de Investigaciones en Catalisis y Petroquimica, Universidad Nacional del Litoral, Santa Fe, ARGENTINA
LARRY ROMSTED, Department of Chemistry, Rutgers University, Piscataway N.J., USA

GILBERTO FERNANDES DE SÁ, Departamento de Quimica Fundamental, Universidade Federal de Pernambuco, Recife, PE, BRASIL

DIMITRIOS SAMIOS, Instituto de Quimica, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, BRASIL
DIOGENES DOS SANTOS, Department of Molecular Biology, Oxford University, Oxford, ENGLAND
JOSEPH A. SCHUFLE, Department of Chemistry, New Mexico Highlands University, Las Vegas, N.M., USA
BEN K. SELINGER, Department of Chemistry, Australian National University, Canberra, AUSTRALIA
KOZO SHINODA, Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokohama, JAPAN
CRISTOFOR I. SIMIONESCU, Academia Romȃna, Filiala Iasi, Iasi, ROMANIA
UMBERTO TONELLATO, Dipartimento di Chimica Organica, Università degli Studi di Padova, Padova, ITALIA

DIETER VOLLHARDT, Max Planck Institut für Kolloid und Grenzflächenforschung, Berlin, GERMANY
RAOUL ZANA, Institut Charles Sadron, CRM-EAHP, Strasbourg, FRANCE

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

ISSN 0104-5431

VOLUME SIX, NUMBER SIX JULY 1998

CONTENTS / CONTEÚDO

A TRIBUTE TO PROFESSOR LAVINEL G. IONESCU
ON HIS 55th BIRTHDAY
UMA HOMENAGEM AO PROF. DR. LAVINEL G. IONESCU
NO SEU 55º ANIVERSÁRIO
A.D. Martinez and B. J. Kid 1

EVALUATION OF AIR QUALITY IN A REGION OF COAL PROCESSING AND SIDERURGIC ACTIVITIES IN THE STATE OF RIO GRANDE DO SUL, BRAZIL
Elba Calesso Teixeira, Josete Dani Sanchez and
Daniela Montanari Migliavacca 11

COMPARATIVE STUDY OF THE CHEMILUMINESCENCE PRODUCED BY THE ACTIVATED POLYMORPHONUCLEAR LEUKOCYTES IN PHYSIOLOGICAL AND VARIOUS PATHOLOGICAL CONDITIONS
R. M. Olinescu, Maria Greabu, D. Crocnan, E.A. Kummerow,
Valy Constantinescu and Fraga Paveliu 25

COMPARATIVE STUDY OF BIOSORPTION OF METALLIC CATIONS BY DIFFERENT BACTERIA
T. Gavriloaiei, Raluca Mocanu, Maria Calistru and
R. Olariu 33

EXTRACTION OF COLORED SUBSTANCES FROM MATÉ (ILEX PARAGUARIENSIS)
Vania Regina Gabbi Polli, Alnei Ramos Prochnow and
Juliane Zimmerman Tamaninini 45

NEW COMPLEXES OF Pr(III), Sm(III), Gd(III), HO(III), La(III) 1-(2'-BENZTHYAZOLYL)-3-METHYL-4-AZO-(4"-NITROPHENYL)-PYRAZOLYN-5-ONE
Anca Emandi, Mariana Balasoiu and Tudor Rosu 53

SnO_2 - BASED INERT ANODES FOR ALUMINIUM ELECTROLYSIS. THE INFLUENCE OF CeO_2 ADDITION ON THE ELECTRICAL RESISTIVITY
Rodica Galasiu, Ioan Galasiu, Niculae Popa and
Vasilica Chivu 63

EFFECTIVENESS OF CERTAIN STABILIZERS ON THE AGEING OF POLYETYLENE FILMS
S. Jipa, R. Setnescu, T. Setnescu, C. Podina and
I. Mihalcea 71

IMMOBILIZATION OF ALCOHOL OXIDASE IN SiO_2 MATRIX PREPARED BY SOL-GEL METHOD
Lia Stanciu, Melania-Liliana Arsene and
Constanta Parlog 77

AUTHOR INDEX 87

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, Nº 6, 1998

A TRIBUTE TO PROFESSOR LAVINEL G. IONESCU ON HIS 55th BIRTHDAY

UMA HOMENAGEM AO PROFESSOR DR. LAVINEL G. IONESCU NO SEU 55° ANIVERSÁRIO

A. D. Martinez
Thunderbird Research Associates
1001 Old Cerillos Road
Santa Fe, New Mexico USA 87500

&

B. J. Kid
Pacific Sunrise Oil Corporation
10800 Wilshire Blvd.
Los Angeles, California USA 90095

ABSTRACT

Professor Lavinel G. Ionescu was born of Romanian parents in Vârset (Vrsac), Banat, Yugoslavia on May 19, 1943. He attended primary and secondary school in Yugoslavia, Italy and Switzerland. He obtained the Bachelor of Science Degree in Chemistry in 1963 and the Master of Science Degree in 1966 from the University of New Mexico, Albuquerque, USA and the Ph.D. Degree in Physical Chemistry from New Mexico State University, Las Cruces, USA in 1970. He did postdoctoral work at the University of California, Santa Barbara and has held faculty positions at universities in the United States and Brazil. At the present, he is Professor of Chemistry at the Pontifícia Universidade Católica do Rio Grande do Sul, Porto Alegre and the Universidade Luterana do Brasil, Canoas, RS, Brazil. His research work includes liquid scintillators, radioactive isotopes, noble gases, solution thermodynamics, surfactants and micelles, micellar catalysis, respiratory pigments, membrane models and history and philosophy of science. He has trained more than fifty research scientists from different parts of the world, is the author of more than two hundred and fifty scientific works and has been the recipient of many prizes and awards.

RESUMO

Professor Dr. Lavinel G. Ionescu nasceu de pais romênos em Vârset (Vrsac), Banat, Iugoslávia em 19 de maio de 1943. Fez os estudos de primeiro e segundo grau na Iugoslávia, Itália e Suiça. Ele obteve o título de B.S. em Química em 1963 e o M.S. em Química em 1966 na University of New Mexico, Albuquerque, USA e o Ph.D. em Físico-Química na New Mexico State University, Las Cruces, USA em 1970. Realizou estudos de pós-doutorado Na University of California, Santa Barbara, USA e ocupou cargos de professor em várias universidades norte-americanas e brasileiras. Na presente data, ele faz parte do corpo docente da Pontifícia Universidade Católica do Rio Grande do Sul e da Universidade Luterana do Brasil, Canoas, RS . As suas atividades de pesquisa incluem cintiladores líquidos, gases nobres, isótopos radioativos, termodinâmica de soluções, surfatantes e micelas, catálise micelar, pigmentos respiratórios, modelos de membranas e história e filosofia da ciência.
O Prof. Dr. L. G. Ionescu preparou mais de cinquenta pesquisadores de várias partes do mundo, é o autor de mais de duzentos e cinqüenta trabalhos científicos e foi honrado com vários prêmios e distinções.

KEYWORDS History of Chemistry, Liquid Scintillators, Noble Gases, Surfactants and Micelles, Micellar Catalysis, Solution Thermodynamics.

DOI: 10.48141/SBJCHEM.v6.n6.1998.4_1998.pdf

A Tribute to Prof. L. G. Ionescu

Uma Homenagem ao Prof. Dr. L. G. Ionescu

Professor Lavinel G. Ionescu was born of Romanian parents on May 19, 1943 in Vârset - Vrsac, Banat, Yugoslavia. He attended primary and secondary school in Sâmianas (Barite), Alibunar and Uzdin, Banat, Yugoslavia and completed high school in Rohrbach bei Huttwil, Bern, Switzerland and Trieste, Italy.

He began his university studies in 1959 at Compton College, Compton, California, where he obtained the Associate in Arts Degree - *Cum Laude* in 1961. Subsequently, he attended the University of California at Los Angeles and obtained the Bachelor of Science Degree with a Major in Chemistry and Minor in Mathematics *With Honors* in 1964 from the University of New Mexico, Albuquerque, USA.

Prof. Dr. L. G. Ionescu obtained the Master of Science Degree with a Major in Physical Organic Chemistry and Minor in Physics from the University of New Mexico in 1966. His M.S. Thesis work dealt with the use of dihydronaphthalenes and dihydrophenanthrenes as liquid scintillators and was done under the supervision of Professors Guido H. Daub and Francis Newton Hayes of the Los Alamos National Scientific Laboratory.

Professor L. G. Ionescu obtained the Doctor of Philosophy Degree with a Major in Physical Chemistry and Minors in Astrophysics and Biology from New Mexico State University, Las Cruces, USA in 1970. His Ph.D. Dissertation dealt mainly with solution thermodynamics, included the study of the interaction of leguminuous hemoglobin with nitrogen and xenon, the properties of the xenon-water clathrate and the solubility of gases and was performed under the supervision of Professor Gordon J. Ewing.

Dr. L. G. Ionescu did postdoctoral work at New Mexico State University and the University of California, Santa Barbara, where he collaborated with Professor Clifford A. Bunton in the area of aggregation colloids and micellar catalysis. He also attended Medical School.

Professor Lavinel G. Ionescu began his academic career as Teaching Assistant at the University of New Mexico and New Mexico State University and as Technical Assistant at the University of Alabama, Tuscaloosa, USA, positions that he held from 1964 to 1970. During the period of 1972 to 1978 he occupied faculty positions at New Mexico Highlands University, Las Vegas, USA and the University of Detroit, Detroit, Michigan, USA.

In June of 1978, accepting an invitation of the Brazilian Minister of Education and Culture, Dr. L. G. Ionescu went to Brazil and joined the faculty of the Universidade Federal de Santa Catarina in Florianópolis as Full Professor of Chemistry. Together with American and other foreign faculty members, he helped establish the Graduate Program in Physical Chemistry and in Physics at UFSC in Florianópolis.

In 1983, Prof. Dr. Lavinel G. Ionescu moved to Porto Alegre where he became a faculty member of the Universidade Federal do Rio Grande do Sul. He occupied the positions of Full Professor of Materials Science in the School of Engineering and Professor of Chemistry in the Instituto de Química and was instrumental in the establishment of the Doctoral Program in Metallurgical and Materials Engineering and the Master Program in Chemistry. In 1992, after denouncing ecologic crimes, embezzlement of public funds and administrative irregularites he was stripped of all his academic rights and dismissed from the faculty of UFRGS, in an action that had high political, moral and inquisitional connotations and implications.

Soon afterwards, he occupied the positions of Professor of Chemistry at the Universidade Luterana do Brasil, Canoas, RS and the Pontifícia Universidade Católica do Rio Grande do Sul, Porto Alegre, positions that he still holds at the present date.

Professor Dr. Lavinel G. Ionescu nasceu de pais romênos em Vârset - Vrsac, Banat, Iugoslávia no dia de 19 de maio de 1943. Ele fez os estudos de primeiro e segundo grau em Sâmianas (Barite), Alibunar e Uzdin, Banat, Iugoslávia e completou a escola secundária em Rohrbach bei Huttwil, Bern, Suiça e Trieste, Itália.

Começou os estudos universitários em 1959 em Compton College, Compton, California, USA e obteve o grau de *Associate in Arts - Cum Laude* em 1961. Subsequentemente, ele frequentou a University of California at Los Angeles e em 1964 obteve o grau de *Bachelor of Science - Cum Laude* da University of New Mexico, Albuquerque, USA, tendo Química como área principal e Matemática como subespecialidade.

O Prof. Dr. L. G. Ionescu obteve o título de M.S. com especialidade em Físico-Química Orgânica e subespecialidade em Física da University of New Mexico em 1966. A sua tese de mestrado teve como ênfase o uso de dihidronaftalenos e dihidrofenantrenos como cintiladores líquidos e foi elaborada sob a orientação dos Professores Guido H. Daub e Francis Newton Hayes do Los Alamos National Scientific Laboratory.

O Prof. Dr. L. G. Ionescu obteve o título de Ph.D. em Físico-Química, tendo como materias secundárias Astrofísica e Biologia, da New Mexico State University, Las Cruces, USA em 1970. O seu trabalho de doutorado tratou principalmente da termodinâmica de soluções, incluindo o estudo da interação da hemoglobina leguminosa com nitrogênio e xenônio, as propriedades do clatrato xenônio-água e a solubilidade de gases e foi executado sob a orientação do Prof. Dr. Gordon J. Ewing.

O Dr. Lavinel G. Ionescu fez estudos de pós-doutorado na New Mexico State University e na University of California, Santa Barbara, USA, onde colaborou com of Prof. Dr. Clifford A. Bunton na área de colóides de associação e catálise micelar. Ele também estudou medicina.

O Prof. Dr. Lavinel G. Ionescu começou a sua carreira acadêmica como Auxiliar de Ensino e Auxiliar Técnico na University of New Mexico, New Mexico State University e University of Alabama, Tuscaloosa, USA, cargos que ele desempenhou entre 1964 e 1970. No período de 1972 a 1978 ele ocupou cargos de Professor na New Mexico Highlands University, Las Vegas, USA e na University of Detroit, Detroit, Michigan, USA.

Em Junho de 1978, aceitando um convite do Ministro da Educação e Cultura, o Dr. Lavinel G. Ionescu veiou para o Brasil e ocupou o cargo de Professor Titular em Química na Universidade Federal de Santa Catarina em Florianópolis. Junto com outros professores americanos e professores estrangeiros, ele ajudou establecer os Programas de Pós-Graduação em Físico-Química e em Física na UFSC.

Em 1983, o Prof. Dr. Lavinel G. Ionescu mudou-se para Porto Alegre e começou a fazer parte do corpo docente da Universidade Federal do Rio Grande do Sul. Ocupou os cargos de Professor Titular de Ciências de Materiais na Escola de Engenaria e Professor Titular de Química no Instituto de Química e teve um papel muito importante no estabelecimento do Programa de Doutorado em Engenharia Metalúrgica e dos Materiais e do Programa de Mestrado em Química. Em 1992, depois de denunciar o Crime Ecológico do Campus do Vale, desvio de dinheiro público e várias irregularidades administrativas, todos os seus direitos acadêmicos foram cassados e ele foi demitido da UFRGS. Isto foi uma ação que teve conotações altamente políticas, morais e inquisitoriais e aconteceu num período de plenas liberdades "democráticas".

Logo após a sua demissão, o Prof. Dr. Lavinel G. Ionescu aceitou os cargos de Professor de Química e Bioquímica da Universidade Luterana do Brasil, Canoas, RS e Professor de Química da Pontifícia Universidade Católica do Rio Grande do Sul, Porto Alegre, funções que ocupa até a presente data.

PROFESSOR DR. LAVINEL G. IONESCU

He has been Visiting Professor at the University of California, Santa Barbara, Universidade de Caxias do Sul, Universidade Regional de Blumenau, Universidade Federal de Santa Maria, Instituto Luterano de Ensino Superior de Manaus, Amazonas and other universities in various continents.

During almost three decades as faculty member at various universities, Prof. L. G. Ionescu participated of a wide number of committees. He was a member of the Library Committee at New Mexico Highlands University (NMHU), the University of Detroit (UofD) and the Universidade Federal do Rio Grande do Sul (UFRGS), Extension, Academic Standing and Scolarship Committees at NMHU, UofD, UFSC and UFRGS and Graduate Committees at all the universities were he held positions. He was Chairman of the Physical Chemistry Division at UFSC, Chairman and Founder of the Catalysis Group at UFRGS, Director of the Laboratory of Surface Chemistry at UFSC and UFRGS and Research Coordinator for the area of Physical Chemistry at UFSC.He served on the Departmental Council and Faculty or College Councils at various universities.

In terms of didactic activities, Prof. L. G. Ionescu teaches or taught mainly courses in physical chemistry at all levels and occasionally general chemistry for freshmen students, biochemistry, quantum mechanics and history and philosophy of science. He was the first scientist in Brazil to offer a formal course on matter and materials under extreme conditions.

Professor L. G. Ionescu's research activities include liquid scintillators, fluorescence, uses and properties of radioactive isotopes of iron and thorium, solution thermodynamics, noble gases, particularly helium and xenon, clathrates or gas hydrates, respiratory pigments, phosphate esters, surfactants and micelles, micellar catalysis, membrane models and history and philosophy of science. He has trained more than fifty (50) research scientists from all continents, is the author of approximately two hundred and fifty (250) scientific publications and has written various short monographs. Some representative publications are given at the end of this article.

Among his more important contributions are the thermodynamic study of the xenon-water clathrate, the study of the micellization process in nonaqueous polar solvents such as glycerol, ethylene glycol and formamide, the effect of cosolvents on micelle formation in water, a micelle model, first proposed during the 174th American Chemical Society National Meeting in Chicago, Illinois in 1977, a classification of solvents using micelles as probes, the interaction of porphyrins with surfactants and micellar catalysis under non-conventional conditions.

We had the privilege to know and collaborate with Prof. L. G. Ionescu, especially during his tenure at New Mexico Highlands University and the University of Detroit. He is a very hard working and kind person and he is always eager to help others. He has an exagerated sense of justice and is very harsh with those that act irresponsibly and abuse and violate the rules of common sense and human decency.

Prof. L. G. Ionescu is fluent in many European languages including Romanian, Serbo-Croatian, Italian, French, Spanish, Portuguese, Rhaeto-Romanic, German, English and has a reasonable knowledge of Latin, Greek, Albanian, Bulgarian and Russian. At times, he surprises people conversing in Chinese, Japanese, Swahili or Hindi. At the present, he is engaged in learning Guarani, the language spoken by the Indians of Paraguay, Uruguay, Southern Brazil and Northern Argentina.

He is a widely travelled person and his trips included the Arctic Circle, Sonoran Desert, Carpathians, the Andes and Aconcagua, the Islands of the Pacific and the Amazon. His hobbies include stamp collecting, mountain climbing, swimming and astronomy. He is also interested in the history, folklore and traditions of

Ele foi Professor Visitante na University of California, Santa Barbara, Universidade de Caxias do Sul, Universidade Regional de Blumenau, Universidade Federal de Santa Maria, Instituto Luterano de Ensino Superior de Manaus, Amazonas e outras universidades em vários continentes.

Durante quase tres décadas como membro do corpo docente de várias universidades, o Prof. Dr. Lavinel G. Ionescu participou de um número grande de comissões. Fez parte da Comissão para a Biblioteca em New Mexico Highlands University (NMHU), University of Detroit (U of D) e na Universidade Federal do Rio Grande do Sul, (UFRGS), das Comissões de Extensão, Avaliação Acadêmica e Bolsas de Estudo em NMHU, U of D, UFSC e UFRGS e de Comissões de Pós-Graduação em todas as universidades onde ocupou cargos. Foi Coordenador da Divisão de Físco-Química na UFSC, Coordenador e Fundador do Grupo de Catálise da UFRGS, Diretor do Laboratório de Físico-Química de Superfícies na UFSC e na UFRGS e Coordenador da Pesquisa em Físico-Química na UFRGS. Serviu no Conselho Departamental e Conselhos e Congregações de Faculdades e Institutos em várias universidades.

Em termos de atividades didáticas, o Prof. Dr. L. G. Ionescu leciona ou lecionou principalmente disciplinas de Físico-Química em todos os níveis e ocasionalmente química geral para calouros, bioquímica, química quântica, estrutura da matéria e história e filosofia da ciência. Ele foi o primeiro cientista no Brasil a oferecer uma disciplina formal sobre matéria e materiais em condições extremas.

As atividades de pesquisa do Professor Dr. Lavinel G. Ionescu abrangem cristais líquidos, cintiladores líquidos, fluorescência, usos e propriedades de isótopos radioativos de ferro e tório, termodinâmica das soluções, gases nobres, especialmente hélio e xenônio, clatratos ou hidratos de gases, pigmentos respiratórios, ésteres de fosfato, surfatantes e micelas, catálise micelar, modelos de membranas e história e filosofia da ciência. Ele preparou mais de cinquenta (50) pesquisadores de todos os continentes , sendo o autor de aproximadamente duzentos e cinquenta (250) trabalhos científicos e de várias monografias. Algumas publicações representativas estão no fim deste artigo.

Entre as suas contribuições mais importantes estão o estudo termodinâmico do clatrato de xenônio e água, o estudo do processo de micelização em solventes polares não-aquosos como glicerol, etilenoglicol e formamida, o efeito de cossolventes sobre a formação de micelas em água, um modelo de micela, proposto durante o 174th American Chemical Society National Meeting em Chicago, Illinois, USA em 1977, a classificação de solventes usando micelas como sondas, a interação de porfirinas com surfatantes e catálise micelar em condições não-convencionais.

Nós tivemos o privilégio de conhecer e colaborar com o Prof. Dr. L. G. Ionescu, especialmente durante sua permanência em New Mexico Highlands University e University of Detroit. Ele é uma pessoa muito trabalhadora e cortês e está sempre disposto a ajudar a outros. Ele tem um sentido de justiça exagerado e é implacável e severo com aqueles que agem de maneira irresponsável e abusam e violam as regras do bom senso e da decência.

O Prof. Dr. Lavinel G. Ionescu fala muitas línguas européias incluindo romêno, sérvio-croata, italiano, francês, espanhol, português, reto-romano, alemão, inglês e possui um conhecimento razoável de latim, grego, albanês, búlgaro e russo. As vezes, ele surprende as pessoas conversando em chinês, japonês, swahili ou hindu. Na presente data ele está aprendendo guarani, a língua falada pelos Índios do Paraguai, Uruguai, Sul do Brasil e o Norte da Argentina.

many peoples. During his years as a student at the University of New Mexico, he was a member of the Kiva Club - Native American Students Association, a close friend of on of the sons of the Governor of Isleta Indian Reservation and learned a lot about the Pueblo Indians, the Hopis and the Navajos. Later, while at New Mexico State University, besides astronomy, he had a lot of interest in the Mescalero and Jicarilla Apaches and the Tarahumara Indians, high in the mountains of Sierra Madre Ocidental in Chihuahua, Mexico. He prides himself of knowing many of Geronimo's trails and drinking water from Geronimo's fountain.

Professor Lavinel G. Ionescu became widely known throughout Brazil as the *Leader of the Pro-Ecologia Group* of Porto Alegre and Viamão after denouncing the ecologic crime of the Campus do Vale of the Federal University of Rio Grande do Sul and widespread corruption and embezzlement of public funds at the same institution. He appeared on all television channels and many radio programs throughout Brazil and some of his interviews covered entire pages of *Jornal do Brasil*, Brazil's most important newspaper.

On the streets of Porto Alegre, many people recognize him as the "courageous Professor of the Instituto de Química of UFRGS" and in Viamão, city where he lives since 1983, he is considered an almost mythological figure and people address him respectfully as *"Professor"* or *"Professor Lavinel"*. Prof. Dr. Dimitrios Samios, present Dean of the College of Chemistry of the Federal University of Rio Grande do Sul has made public depositions considering him as an *archetype*, a model person or prototype that came to the wrong place at the wrong time and before his time.

When asked about persons that have marked his academic career, Professor L. G. Ionescu always remembers two: Dr. Glenn A. Crosby, currently Professor of Chemistry and Materials Science at Washington State University and Dr. Clyde W. Tombaugh, Discoverer of Pluto, Emeritus Professor of Astronomy at New Mexico State University, Las Cruces. With Crosby he learned quantum chemistry, structure of matter, spectroscopy and statistical mechanics and Tombaugh motivated his interest for astronomy and astrophysics. Both of them were real masters, taught mainly by their example and gave a few glimpses of what life is really about.

Prof. Dr. Lavinel G. Ionescu has received many prizes, distinctions and awards, has given invited lectures in more than twenty different countries and organized or helped organize many scientific events all over the world. Among them we cite the *"Symposium on Chemistry in Latin America"* during the First Chemical Congress of the North American Continent in Mexico City in 1975 various *International Symposia on Surfactants in Solution*.

He is a member of the California Junior Colleges Scolarship Federation, Society of Sigma Xi- Scientific Research Society (USA), Sigma Pi Sigma - National Physics Honor Society (USA), Past President and Vice-President of the Physical Sciences Section of the Michigan Academy of Arts, Science and Letters, New Mexico Academy of Sciences, New York Academy of Sciences, Founding Member of the American Romanian Academy of Arts and Sciences together with Mons. Octavian Bârlea, Mircea Eliade and George Emil Palade, Nobel Laureate in Medicine and Founding President of *SARMISEGETUSA RESEARCH GROUP* of Santa Fe and Las Cruces, New Mexico, USA.

Dr. L. G. Ionescu is a member of the American Chemical Society since 1965, American Association for the Advancement of Science, Astronomical Society of Las Cruces, Sociedade Brasileira de Química, Associação Brasileira de Química, Sociedade Brasileira de Bioquímica e Biologia Molecular, Sociedade Brasileira para o Progresso da Ciência and the Planetary Society and Sociedade Iberoamericana de Cristais Líquidos.

O Prof. Dr. Lavinel G. Ionescu viajou muito e entre as regiões que ele conhece estão o Círculo Polar Árctico, o Deserto de Sonora, os Cárpatos, os Andes e Aconcagua, as Ilhas do Pacífico e a Amazônia. Ele é um colecionador de selos postais, gosta de alpinismo e de natação e adora astronomia. Ele também tem muito interesse na história e folclore tradição de muitos povos. Nos seus anos de estudante na University of New Mexico, ele foi sócio do Kiva Club - Associação dos Estudantes Americanos Nativos e bom amigo de um dos filhos do Governador da Reserva Índia de Isleta e aprendeu muitas coisas sobre os Índios Pueblo, os Hopis e os Navajos. Mais tarde, quando estudava em New Mexico State University, além da astronomia, ele tinha muito interesse para os Apaches das Tribos Mescalero e Jicarilla e os Índios Tarahumara no alto das montanhas da Sierra Madre Occidental em Chihuahua, México. Ele está orgulhoso de conhecer muitas das trilhas de Gerônimo e de ter bebido água da Fonte de Gerônimo.

O Prof. Dr. Lavinel G. Ionescu ficou amplamente conhecido no Brasil todo como o *Leader do Grupo Pró-Ecologia* de Porto Alegre e Viamão depois de denunciar o *Crime Ecológico do Campus do Vale* da Universidade Federal do Rio Grande do Sul e muita corrupção, desvio de dinheiro público e irregularidades administrativas na mesma instituição. Apareceu em todos os canais de televisão e muitos programas de radio no Brasil inteiro e as suas entrevistas as vezes cobriram páginas inteiras do *Jornal do Brasil*, o diário mais importante do País.

Nas ruas de Porto Alegre é reconhecido por muita gente como *"O Professor corajoso do Instituto de Química da UFRGS"* e em Viamão, cidade onde reside desde 1983, ele é considerado uma figura quase mitológica e folclórica e as pessoas se direigem a ele respeitosamente como *"Professor"* ou *"Professor Lavinel"*. O Prof. Dr. Dimitrios Samios, atual Diretor do Instituto de Química da Universidade Federal do Rio Grande do Sul prestou depoimentos públicos onde considera o Prof Lavinel como *arquétipo*, uma pessoa modelo ou protótipo que veiou ao lugar errado no tempo errado e antes da hora certa.

Quando indagado sobre pessoas que marcaram a sua carreira acadêmica, o Professor Lavinel sempre se lembra de duas pessoas: Dr. Glenn A. Crosby, atualmente Professor de Química e Ciências de Materias em Washington State University e Dr. Clyde W. Tombaugh, Descobridor do Planeta Plutão e Professor Emérito de Astronomia em New Mexico State University, Las Cruces. Com Crosby ele aprendeu química quântica, estrutura da matéria, espectroscopia e mecânica estatística e foi Tombaugh que motivou o seu interesse pela astronomia e astrofísica. Os dois foram verdadeiros mestres, ensinaram principalmente pelos seus exemplos e deram alguns vislumbres sobre o propósito da vida.

O Prof. Dr. Lavinel G. Ionescu recebeu muitos prêmios, honrarias e distinções. Ele proferiu palestras e conferências convidadas em mais de vinte paises diferentes e organizou ou ajudou organizar muitos encontros científi- em várias partes do mundo. Entre eles citamos o *"Simpósio Sobre Química na América Latina"* durante o Primeiro Congresso Químico do Continente Norte-Americano na Cidade do Mexico em 1975 e vários *Simpósios Internacionais Sobre Surfatantes em Solução*.

Ele é membro da California Junior Colleges Scolarship Federation, Society of Sigma Xi - Scientific Research Society of America (USA), Sigma Pi Sigma - National Physics Honor Society (USA), Ex-Presidente e Vice-Presidente da Secção de Ciências Físicas da Michigan Academy of Arts, Science and Letters, New Mexico Academy of Science, New York Academy of Sciences, Membro Fundador da American Romanian Academy of Arts and Sciences junto com Mons. Octavian Bârlea, Mircea Eliade e George Emil Palade, Laureado Nobel em Medicina e Presidente Fundador do *SARMISEGETUSA RESEARCH GROUP* de Santa Fe e Las Cruces, Novo México, Estados Unidos.

He acted as Secretary of the Rio Grande do Sul Section of the Brazilian Chemical Society from 1987 to 1990, was Brazilian National Representative in the Commission on Colloid and Surface Chemistry Including Catalysis of the *INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY* (1983-85), Brazilian Representative for the UNESCO Program for Chemistry in Latin America, member of the Escuela Latinoamericana de Química Inorganica, and Consultant of most Brazilian Granting Agencies.

Dr. L. G. Ionescu received the distinctions of Paranymph and Honored Professor from many generations of chemists that graduated from the Universidade Federal do Rio Grande do Sul (UFRGS), Pontifícia Universidade Católica do Rio Grande do Sul (PUCRS) and Universidade Luterana do Brasil (ULBRA).

He is Researcher IA (highest cathegory) of CNPq - National Brazilian Research Council and is included in *American Men and Women of Science, Who is Who, Who is Who in the World, International Who is Who and the World Book of Ionescu's.*

In 1965, after graduating with honors from the University of New Mexico, Governor Tom Campbell declared him an *"Honorary Citizen of the State of New Mexico"* and during his tenure as a young Professor at New Mexico Highlands University, Las Vegas (1972-75). Dr. L. G. Ionescu had close ties with the Governor's Office and Governor Bruce King's Staff.

He is the editor of *QUÍMICO PAMPEANO* and the *SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY* and is a member of the Editorial Board of various journals, including the *BRAZILIAN JOURNAL OF MATERIALS SCIENCE AND ENGINEERING.*

We salute Professor Dr. Lavinel G. Ionescu on the occasion of his fifty-fifth birthday, congratulate him for his effort during the last thirty years and wish him happiness, good health, good will and success for the days ahead.

O Dr. L. G. Ionescu é sócio da American Chemical Society desde 1965, American Association for the Advancement of Science, Astronomical Society of Las Cruces, Sociedade Brasileira de Química, Associação Brasileira de Química, Sociedade Brasileira de Bioquímica e Biologia Molecular, Sociedade Brasileira para o Progresso da Ciência, The Planetary Society e da Sociedade Iberoamericana de Cristais Líquidos.

Ele desempenou a função de Secretario Regional da Sociedade Brasileira de Química de 1987 a 1990, foi Representante Nacional do Brasil na *Commission on Colloid and Surface Chemistry Including Catalysis da INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY (IUPAC)* de 1983 a 1985, Representante do Brasil no Programa de Química da UNESCO para América Latina, membro da Escuela Latinoamericana de Química Inorganica e Consultor da maiora das agências de fomento à pesquisa no Brasil.

O Prof. Dr. Lavinel G. Ionescu foi Paraninfo e Professor Homenageado de muitas turmas de químicos formados na Universidade Federal do Rio Grande do Sul, Pontifícia Universidade Católica do Rio Grande do Sul e na Universidade Luterana do Brasil.

Ele é Pesquisador IA(categoria mais alta) do CNPq- Conselho Nacional de Desenvolvimento Científico e Tecnológico e seu nome está incluido em *American Men and Women of Science, Who is Who, Who is Who in the Wolrd, International Who is Who* e *The World Book of Ionescu's.*

Em 1965, depois de se formar *Cum Laude* na University of New Mexico, o Governador Tom Campbell declarou o Dr. L. G. Ionescu *"Cidadão Honorário do Estado do Novo México"* e durante a sua permanência como jovem professor na New Mexico Highlands University, Las Vegas (1972-75) ele teve ligações estreitas com o Gabinete do Governador Bruce King e o seu Secretariado.

Ele é editor do *QUÍMICO PAMPEANO* e do *SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY* e faz parte do Corpo Editorial de várias revistas e periódicos, incluindo o *BRAZILIAN JOURNAL OF MATERIALS SCIENCE AND ENGINEERING.*

Saudamos o Prof. Dr. Lavinel G. Ionescu na ocasião do seu 55º aniversário, o felictamos e parabenizamos pelo seu esforço durante os ultimos trinta anos e lhe desejamos felicidade, saúde, boa vontade e êxito nos anos vindouros.

REPRESENTATIVE PUBLICATIONS
TRABALHOS REPRESENTATIVOS

1. Lavinel G. Ionescu, *Liquid Scintillators. Some 3-Aryl-1,2-Dihydronaphthalenes, 3-Aryl-1,2-Dihydro-4-Methylnaphthalenes, 3-Aryl-1,2-Dihydrophenanthrenes and 3-Aryl-1,2-Dihydro-4-Methylphenanthrenes . Steric Effects of the Methyl Group,* Master's Thesis, University of New Mexico, Albuquerque, USA, 112 pp.,1965. (Work supported by the United State Atomic Energy Commission).

2. Lavinel G. Ionescu, *Attempts to Study the Interaction of Leguminous Hemoglobin with Nitrogen and Xenon,* Doctoral Dissertation, New Mexico State University, Las Cruces, USA, 1970, 178 pp., *Dissertation Abstracts Intl., B 31(5), 2603 (1970).* (Work supported by the National Science Foundation).

3. G. H. Daub, F. N. Hayes, D. W. Holty, L. Ionescu and J. L. Schornick, Liquid Scintillators XIV. The Synthesis and Evaluation of Some trans-1,2-Diarylethylenes as Liquid Scintillators, The Steric Effects of a Methyl Group., *Molec. Liquid Crystals, 4,* 343-355 (1968).

4. G. J. Ewing and L. G. Ionescu, The Interaction of Leghemoglobin with Nitrogen and Xenon, *J. Phys. Chem. 76,* 591-596 (1972).

5. C. A. Bunton and L. G. Ionescu, Hydrolysis of Di- and Trisubstituted Phosphate Esters Catalyzed by Nucleophilic Surfactants, *J. Amer. Chem. Soc., 95,* 2912-2917 (1973).

6. L. G. Ionescu, Some Aspects of the Chemistry of Xenon and Other Noble Gases, *Rev Roum. Chim., 18,* 1731-1747 (1973).

7. G. J. Ewing and L. G. Ionescu, The Dissociation Pressure and Other Thermodynamic Properties of the Xenon-Water Clathrate, *J. Chem. Eng. Data, 19,* 367-369 (1974).

8. C. A. Bunton, S. Diaz, J. M. Hellyer, Y. Ihara and L. G. Ionescu, Micellar Effects upon the Reactions of 2,4-Dinitrophenyl Phosphate and Ethyl p-Nitrophenyl Phosphate with Amines, *J. Org. Chem., 40,* 2313-2317 (1975).

9. L. G. Ionescu, Teaching Introductory Chemistry in Spanish to Bilingual Students, *J. Chem. Educ., 53,* 250 (1976).

10. G. J. Ewing and L. G. Ionescu, Exchange of Leguminous Hemoglobin with Radioactive Iron, *Rev. Roum. Biochim., 13,* 193-195 (1976).

11. J. A. Schufle and L. G. Ionescu, Fritz Feigl - Brazil's Spot Tester, *J. Chem. Educ., 53,* 174 (1976).

12. L. G. Ionescu, The Entropy of Some Simple Gas-Water Clathrates, *Rev. Roum. Chim., 23,* 45-53 (1978)

13. L. G. Ionescu, Some Romanian Contributions in Astronomy, *St. Nicholas Bulletin (Detroit), 29,* 3-6 (1978).

14. L. G. Ionescu, Purification of Water with Clathrates, *N. Mex. J. Sci., 18(2),* 22-24 (1978).

15. L. G. Ionescu and J. A. Schufle, José Luis Casaseca, Founder of the Cuban Institute of Chemical Research, *J. Chem. Educ., 55,* 583 (1978).

16. L. G. Ionescu and J. K. Tsang, Interaction of Ferrimyoglobin with Surfactants, *Rev. Roum. Biochim., 15,* 211-218 (1978).

17. L. G. Ionescu, T. Tokuhiro and B. J. Czerniawski, Formation of Micelles of Cetyltrimethylammonium Bromide in Water-N,N-Dimethylformamide Solutions, *Bull. Chem. Soc. Japan, 52,* 922-924 (1979).

18. T. Tokuhiro, L. G. Ionescu and D. S. Fung, Effect of Intermolecular Interactions on the Formation of Micelles. Proton Spin-Lattice Relaxation Study in Water-Dimethylsulfoxide Solutions of Hexadecyltrimethylammonium Bromide, *J. Chem. Soc. Faraday Trans. II, 75,* 975-984 (1979).

19. L. G. Ionescu, T. Tokuhiro, B. J. Czerniawski and E. S. Smith, Formation of Micelles of Cetrytrimethylammonium Bromide in Water-Dimethylsulfoxide Solutions, in *Solution Chemistry of Surfactants, Vol. 1,* K. L. Mittal, Ed., Plenum Press, New York, USA, 1979, p. 487-496.

20. T. Tokuhiro and L. G. Ionescu, Temperature Effect on Molecular Dynamics in Micellar System. Proton Spin-Lattice Relaxation Study of Cetyltrimethylammonium Bromide in Water-Dimethysulfoxide Mixtures, in *Solution Chemistry of Surfactants, Vol. 1,* K. L. Mittal, Ed., Plenum Press, New York, USA, 1979, p. 497-506.

21. L. G. Ionescu and A. R. Lopez, Chemical Analysis of Water Samples of the El Rito River, Rio Arriba County, N. Mexico, *N. Mex. J. Science, 20(1),* 8-11 (1980).

22. L. G. Ionescu, Romanians in the History of Mexico, in *America Almanach,* P. Lucaci, Ed., Union and League of Romanian American Societies, Inc., Cleveland, Ohio, USA, 1980, p. 156-162.

23. F. Nome. E. W. Schwingel and L. G. Ionescu, Micellar Effects on the Base Catalyzed Oxidative Cleavage of a Carbon-Carbon Bond in 1,1-bis(p-Chlorophenyl)-2,2,2-Trichloroethanol, *J. Org. Chem., 45,* 705-711 (1980).

24. L. G. Ionescu and J. A. Schufle, Alvaro Reynoso - Father of Cuban Sugar Technology, *N. Mex. J. Science, 21(1),* 41-43 (1981).

25. L. G. Ionescu and B. J. Czerniawski, Interaction of Ferriprotoporphyrin IX with Cetyltrimethylammonium Bromide, *Rev. Roum Biochim., 18,* 103-111 (1981).

26. L. G. Ionescu and D. S. Fung, Formation of Micelles of Acylcarnitines in Glycerol, *Bull. Chem. Soc. Japan, 54,* 2503-2506 (1981).

27. L. G. Ionescu and D. S. Fung, Formation of Micelles of Acylcarnitine Chlorides in Ethylene Glycol, *J. Chem. Soc. Faraday Trans. I, 77,* 2907-2912 (1981).

28. L. G. Ionescu and V. T. De Favere, Formation of Micelles of Cetrytrimethylammonium Bromide in Solutions of Water-Acetone, in *Solution Chemistry of Surfactants -Theoretical and Applied Aspects, Vol. 1,* K. L. Mittal and E.J. Fendler, Eds., Plenum Press, New York, USA, 1982, p. 407-416.

29. F. Nome. A. Neves and L. G. Ionescu, Specific Role of Functional Micelles in the Catalysis of an Elimination Reaction, in *Solution Chemistry of Surfactants - Theoretical and Applied Aspects, Vol. 2,* K. L. Mittal and E.J. Fendler, Eds., Plenum Press, New York, USA, 1982, p. 1157-1170.

30. L. G. Ionescu, R. A. Yunes and J. A. Schufle, Horacio Damianovich, Argentine Pioneer in Noble Gas Chemistry, *J. Chem. Educ., 59,* 304 (1982).

31. F. Nome, A. Rubira, C. Franco and L. G. Ionescu, Limitations of the Pseudo-Phase Model of Micellar Catalysis. The Dehydrochlorination of DDT and Some of Its Derivatives, *J. Phys. Chem., 86,* 1181-1185 (1982).

32. L. G. Ionescu, L. S. Romanesco and F. Nome, The Effect of Cosolvents on the Formation of Micelles of Cetyltrimethylammonium Bromide in Aqueous Solutions, in *Surfactants in Solution, Vol. 2,* K. L. Mittal and B. Lindman, Eds., Plenum Press, New York, USA, 1984, p. 789-804.

33. L. G. Ionescu and F. Nome, On the Validity of the Pseudo-Phase Model of Micellar Catalysis, in *Surfactants in Solution, Vol.1,*K, L. Mittal and B. Lindman, Eds., Plenum Press, New York, USA, 1984, p. 1107-1120.

34. L. G. Ionescu, Quasi-Elastic Light Scattering of Cetyltrimethylammonium Bromide in Aqueous Salt Solutions, *Quim. Nova, 8(3),* 191-192 (1985).

35. L. G. Ionescu, The Effect of Additives on the Formation of Micelles in Aqueous Solutions, *Contrib. Cient, Tecnol. Santiago (Chile), NS,* 35-39 (1985).

36. L. G. Ionescu, *Estudo de Sistemas Micelares por Espalhamento Quase-Elástico de Luz,* Monografia, Universidade Federal do Rio Grande do Sul, Porto Alegre, 1985, 45 pp.

37. D. H. Everett, L. G. Ionescu and Other Members of the IUPAC Commission on Colloid and Surface Chemistry Including Catalysis, Reporting Data on Adsorption at the Solid/Solution Interface, *Pure & Appl. Chem., 58(7),* 967-984 (1986).

38. L. G. Ionescu, M. J. B. Miguez and B. J. Kid, Failure of the Pseudo-Phase Model of Micellar Catalysis. Decomposition of a Phosphate Esterin the Presence of Cetyltrimethylammonium Chloride (CTACl), *Atual. Fis. Quim. Org., 2.* 89-102 (1986).

39. L. G. Ionescu, *Teoria de Combinação Linear de Orbitais Atômicos - Orbitais Moleculares*, Monografia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, 1987, 44pp.

40. L. G. Ionescu and N. A. Wiederkehr, Interaction of Magnesium Phthalocyanines with Organic Solvents, *Quim. Nova, 10(3)*, 246-248 (1987).

41. L. G. Ionescu and C. C. Moro, Determination of Chlorinated Organic Compounds in Effluents of Cellulose Pulp from Southern Brazil, *Quim. Nova, 12(1)*, 108-110 (1989).

42. L. G. Ionescu, T. H. M. Do Aido and B. J. Kid, Aggregation of Cetyltrimethylammonium Bromide (CTAB) in Aqueous Solutions Containing Sodium Chloride, *Bol. Soc. Chil. Quim., 35*, 105-111 (1990).

43. L. G. Ionescu, Editor, *Proceedings of the Second Symposium on Philosophy and History of Science - Anais do 2º Simpósio de História e Filosofia da Ciência*, Sociedade Brasileira de Química - Regional do Rio Grande do Sul, Editora Químico Pampeano, Viamão, RS, Brasil, 1990, 76 pp.

44. L. G. Ionescu, *Astroquímica - Uma Área Nova, Fascinante e Interessante da Química*, Monografia, Universidade Federal de Pernambuco, Recife, PE, Brasil, 1991, 12 pp.

45. L. G. Ionescu, Xorge Alejandro Dominguez, Mexico's Foremost Organic Chemist, *South. Braz. J. Chem., 2*, 1-4 (1994).

46. A. Müller, J. L. S. Barcelos and L. G. Ionescu, Use of Surfactants Added to Refractory Slurry in Precision Foundry and Investment Castings with Aluminum, *South. Braz. J. Chem., 2*, 41-54 (1994).

47. L. G. Ionescu and E. F. De Souza, Internal Pressure of Liquids and the Rate of a Micellar Catalyzed Reaction, *South. Braz. J. Chem., 3*, 63-78 (1995).

48. L. G. Ionescu and E. F. De Souza, Micellar Catalyzed Reactions in Mixed Solvent Systems, in *Surfactants in Solution, Vol. 64*, K. L. Mittal and A. K. Chattopadhyay, Eds., Marcel Dekker Inc., New York, N.Y., USA, 1996, p. 123-132.

49. L. G. Ionescu, *Descoberta, Propriedades e Usos do Hélio no Mundo Moderno*, Monografia, Universidade de Cruz Alta, Cruz Alta, RS, Brasil, 1998, 18pp.

50. L. G. Ionescu, S. M. Hickel Probst and E. F. De Souza, Formation of Micelles of Cetyltrimethylammonium Bromide in Water-Glycerol Solutions, *South. Braz. J. Chem., 6(7)*, 67-76 (1998).

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, Nº 6, 1998

EVALUATION OF AIR QUALITY IN A REGION OF COAL PROCESSING AND SIDERURGIC ACTIVITIES IN THE STATE OF RIO GRANDE DO SUL, BRAZIL

Elba Calesso Teixeira[1]; Josete Dani Sanchez[2] and Daniela Montanari Migliavacca[1]

[1]Fundação Estadual de Proteção Ambiental do Rio Grande do Sul.
Rua Carlos Chagas, 55/707- CEP : 90030-020 - Porto Alegre -RS

[2]Fundação de Ciência e Tecnologia do Rio Grande do Sul
Rua Washington Luiz,675 - CEP: 90010-460 - Porto Alegre - RS

ABSTRACT

The present work involved the determination of total suspended particles, SO_2 e NO_2 in the municipalities of Charqueadas and São Jerônimo, Rio Grande do Sul, Brasil. The area is marked by the presence of coal-fired power stations and siderurgic activities. The gases SO_2 and NO_2 do not affect air quality, but the results revealed contamination of air in Charqueadas due to total suspended particles. The presence of Fe, Mn, Cu, Cr and Ni, is probably due to the steel industry. On the other hand, Pb and part of Cu and Ni can be attributed to the coal- fired power station.

RESUMO

O presente trabalho envolveu a detreminação de partículas totais em suspensão, SO_2 e NO_2 nos municípios Charqueadas e São Jerônimo, Rio Grande do Sul, Brasil. Na área está inserida duas termolétricas e uma siderúrgica. Os gases SO_2 e NO_2 não afetam a qualidade do ar, mas os resultados revelaram contaminação do ar em Charqueadas devido a partículas totais em suspensão. A presença de Fe,Mn, Cu, Cr e Ni são, provavelmente, originários da indústria siderurgia. Por outro lado, podem ser atribuído a presença de Pb e, também em parte de Cu e Ni pode ser atribuído a termoelétrica.

KEYWORDS: Air Quality, Sulfur Dioxide, Nitrogen Dioxide, Suspended Particles, Heavy Metals.

DOI: 10.48141/SBJCHEM.v6.n6.1998.14_1998.pdf

INTRODUCTION

The purpose of the present work is to contribute to the understanding of air quality in the State of Rio Grande do Sul, Brazil, evaluating the environmental impact caused by coal processing and steel production activities and determine the parameters that are indicatives of air pollution: SO_2, NO_2, total suspended particles and associated metals. The region, chosen for this study was the Baixo Jacuí(Lower Jacuí River) including the municipalities of Charqueadas and São Jerônimo.

The use of fossil fuels for energy generation, including coal, is a major source of emission of particulate pollutants, SO_2 and NO_2. The concentration these pollutants depend on the characteristics of the coal (ash and sulfur contents) and on the combustion process employed.

Problems related to the emission of pollutants are not always solved by a modification of the combustion process or by the use of controlling devices used to attend standards required by specific legislation of each country.

This legislation varies significantly from country to country and tends to be more restrictive as far as air quality standards are concerned. Atmospheric pollutants are a major challenge for Brazilian and world wide agencies of environmental protection since they still surpass legal limit values of air quality standards and the satisfactory reduction of their concentration in metropolitan areas has still to be achieved.

In Southern Brazil, particulate matter and SO_2 are the object of particular concern, since their emission levels are usually high, when compared to standards of other countries. This is mainly due to the lack of controlling devices for SO_2 and the low efficiency of the systems used for fine particles, which are generally metal enriched and pose a great risk to human heath.[1-5]

The large scale use of coal in electric energy generation has caused serious alterations in the atmospheric environmental quality in various areas of the state of Rio Grande do Sul, Brazil. One of them is the Baixo Jacuí River Basin, marked by the presence of coal-fired power stations, siderurgic industries and deposit of coal and ash wastes. The implantation of a new coal-fired power station (Jacuí I) will increase even more the coal combustion and in all probability will also aggravate the atmospheric contamination.

EXPERIMENTAL

Air samples were collected during the period of May 1994 to November 1995 on every sixth day using a procedure proposed by the United States Environmental Protection Agency (USEPA)[6]. Sulfur dioxide, nitrogen dioxide were collected using high volume gas (Tri-Gas) and total suspend particles (Hi-Vol) samplers. Samplings were done at three different sites: two in the municipality Charqueadas and one in the municipality São Jerônimo (see Figure 1). The selection of these sites followed various criteria and included the distance from the sources of pollution, the proximity to the center of the two towns and the preferential direction of the winds.

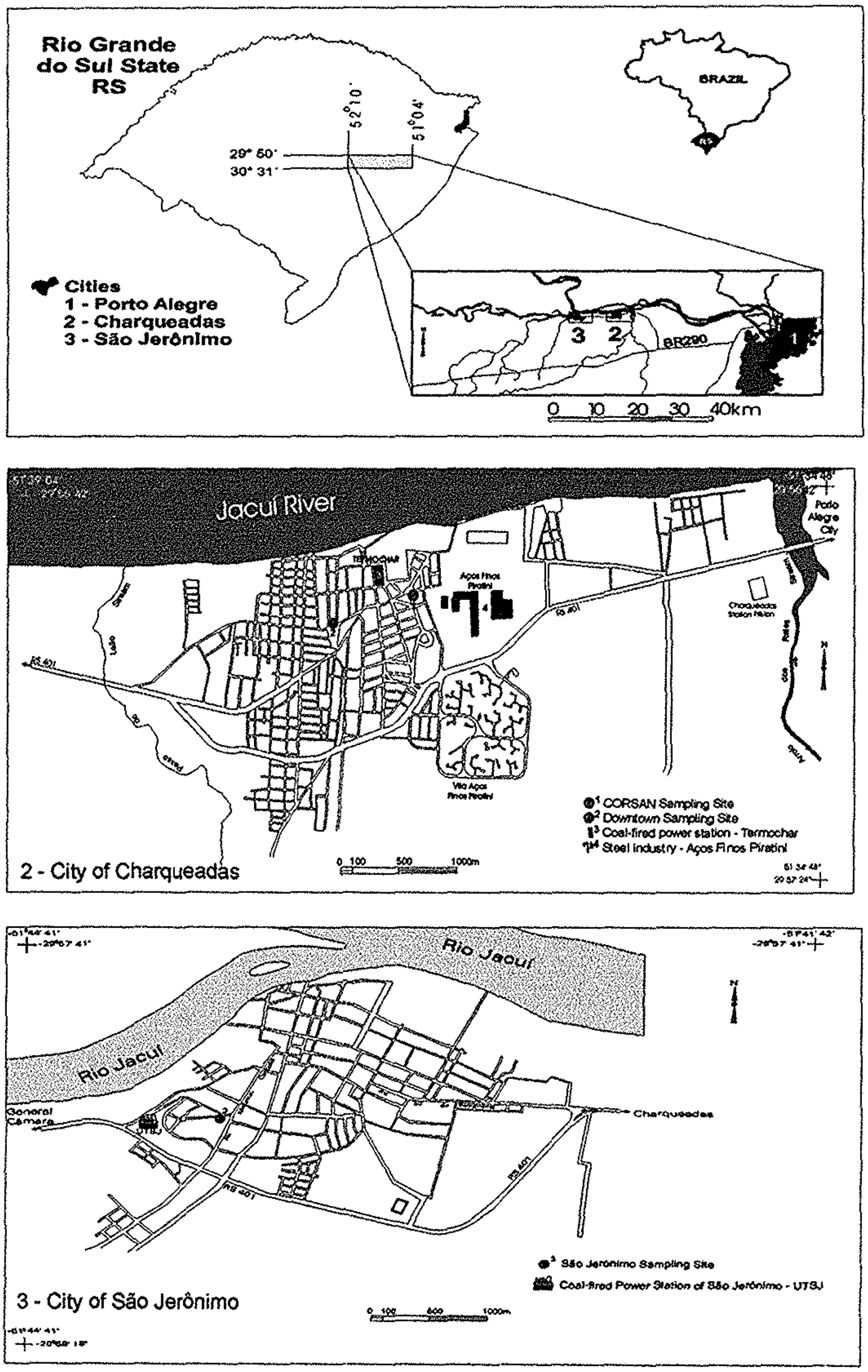


Figure 1. Location of Air Sampling Sites - Charqueadas and São Jerônimo Municipalities, State of Rio Grande do Sul, Brazil.

Sulfur and nitrogen dioxide were determined, respectively, by the pararosaniline method[6] and by a colorimetric method based on sodium arsenite, recommended by the United States Environmental Protection Agency[7]. The concentration of total suspended particles was determined according to a procedure given by the same agency[8].The study of the metals associated to particulate matter, collected with July 1994, started with the preparation of samples that consisted of dividing the filter in to four equal parts and analyzing only one of them. The extraction of the metals was done according to a procedure described by Sanchez and collaborators[9] and consisted of extracting the metals from the filter paper, adding 20 ml of concentrated HNO_3 and 20 ml of 30% H_2O_2 into a flask provided with a reflux condenser and heating in a steam bath. Subsequently, aliquots of 30 ml of concentrated HCl and 10 ml of concentrated HNO_3 were added in diferent steps until the complete elimination of organic matter. The determination of metals (Fe, Mn, Cu, Pb, Cr, Ni, Co e Cd) present in the extracts was performed by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Gases: SO_2 and NO_2. Sulfur dioxide concentrations measured over a period from May 1994 to November 1995 are shown in Figure 2. These results are compared to air quality standards established by Brazilian Legislation[10]. As an be seen, the SO_2 concentrations at the three sites were generally low and surpassed the secondary standards value(100 $\mu g\ m^{-3}$) only at the CORSAN (Water Company Treatment Plant), sampling site in Charqueadas, localized close to anthropogenic sources - the steel plant and coal-fired power station. The anomaly was verified only on three specific dates (September 30, 1994; October 24,1994 and April 1, 1995) when maximum values reached 118 $\mu g\ m^{-3}$, 212.2 $\mu g\ m^{-3}$e 174.2 $\mu g\ m^{-3}$, respectively. The experimental annual mean value for SO_2 concentration was inferior to the primary annual standard (80 $\mu g\ m^{-3}$) for all sampling sites.

On the other hand, the mean measurement to at the CORSAN sampling site in Charqueadas (64.4 $\mu g\ m^{-3}$) surpassed the annual mean secondary standards(40$\mu g\ m^{-3}$), indicating a slight alteration of air quality, which is likely to worsen with the installation of the new coal-fired power station (Jacuí I) at a nearly location. Data of the present study are in good agreement with those obtained by the JICA/ELETROSUL/CEEE (Japan International Cooperation Agency/ Centrais Elétricas do Sul do Brasil/ Companhia Estadual de Energia Elétrica - RS)[11] monitoring that reveals that the air quality in the Charqueadas Municipal has not altered by SO_2.

Figure 3 illustrates the concentrations determined for NO_2 *during the period of* May 21,1994 to November 11,1995 at the three sampling stations. The results are compared to the German Standards[12], since Brazilian Legislation[10] does not establish concentration limits for NO_2 for a 24 hour sampling period. In general, the concentrations obtained for NO_2 were low, fluctuated during the period under considerations and the annual average was inferior to the German Standard (100μgm^{-3})[12]. These results agree with those obtained by the

JICA/ELETROSUL/CEEE[11] monitoring study performed in Charqueadas and suggest that there is no alteration of the air quality due to NO_2 from local sources.

Total Suspended Particles. Figure 4 illustrates the results obtained for the concentration of total suspended particles for same period described above and for the three sampling locations. These results are compared to air quality standards specified by Brazilian Legislation[10]. Results obtained for the CORSAN sampling station in Charqueadas contained values that surpassed nine times the primary standard (240 µg m^{-3}) set by Brazilian Legislation and twenty four times the secondary standard *(150 µg m^{-3}) during the period under consideration. For the Downtown sampling site in* Charqueadas, elevated values of total suspended particles were also obtained although they are less significant than those of the CORSAN location. At the Downtown sampling site, the concentration of particulates surpassed the primary standard only one occasion (September,24 1994) and the secondary standard on the different opportunities.

Mean geometrical annual averages for the CORSAN and Downtown stations in Charqueadas were superior to both annual primary and secondary standards, 80 µg m^{-3} and 60 µg m^{-3}, respectively. These results show the air quality contamination by total suspended particles, suggesting a strong contribution of emission of local sources such as the coal-fired power stations (TERMOCHAR) and particularly the steel plant (Aços Finos Piratini). This siderurgic has no control for emission[13] and the atmospheric pollution can be verified visually by the reddish color of the smoke, the city of São Jerônimo dues not yet present serious problems of atmospheric contamination by particulate material. However, on certain dates (April 24, 1995 and May 28,1995) we measured concentration of particulate above the secondary standards (150 µg m^{-3})[10]. This was probably due to anthropogenic factor located in Charqueadas (coal-fired power station and steel industry) and the direction of the winds on those days.

Metals associated with suspended particles. Table 1 summarizes geometrical means, maximum and minimum values for metals associated with total suspended particles at the three sites studied for the periods of June 21,1994 to November 17,1995. Of all the metals studied, Fe presented the highest concentration at all sites, the most elevated values being those detected at the Charqueadas CORSAN station. The emission of iron oxide associated with particulate material could be visually detected by the reddish color in the smoke of the steel industry.

The concentration of the other elements studied was also more elevated at the CORSAN station, except for Cr and Ni that presented higher values at the Downtown Charqueadas sampling site on certain days. This difference can be explained by horizontal movement of air masses containing these elements in association with finer suspended particles, that remain in suspension in air for move prolonged periods of time.

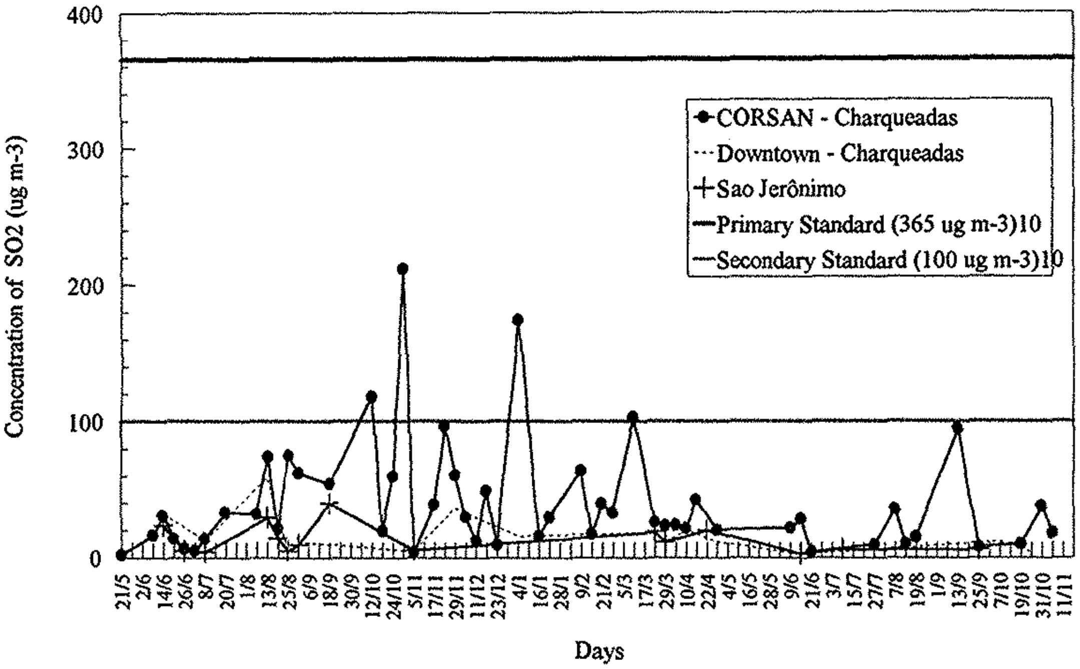


Figure 2. Concentrations of SO_2 ($\mu g\ m^{-3}$) determined during the period of May 1994 to November 1995 for the three sites studied in of Charqueadas and São Jerônimo.

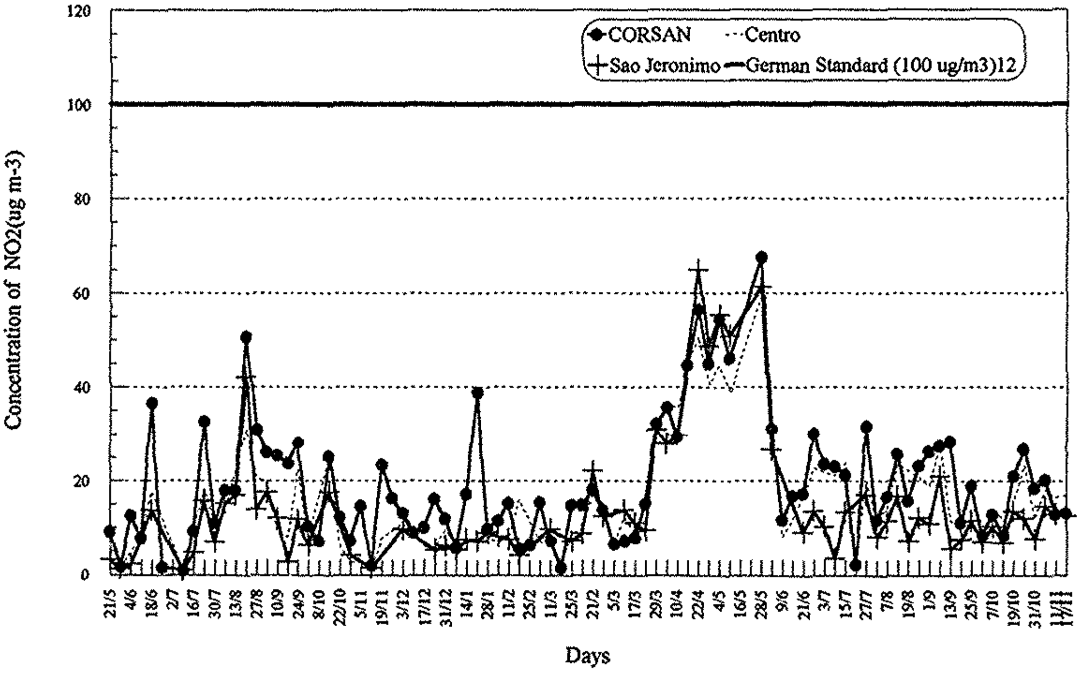


Figure 3. Concentration of NO_2 ($\mu g\ m^{-3}$) *determined during the period of May 1994 to November 1995 for the three sampling stations in of Charqueadas and São Jerônimo.*

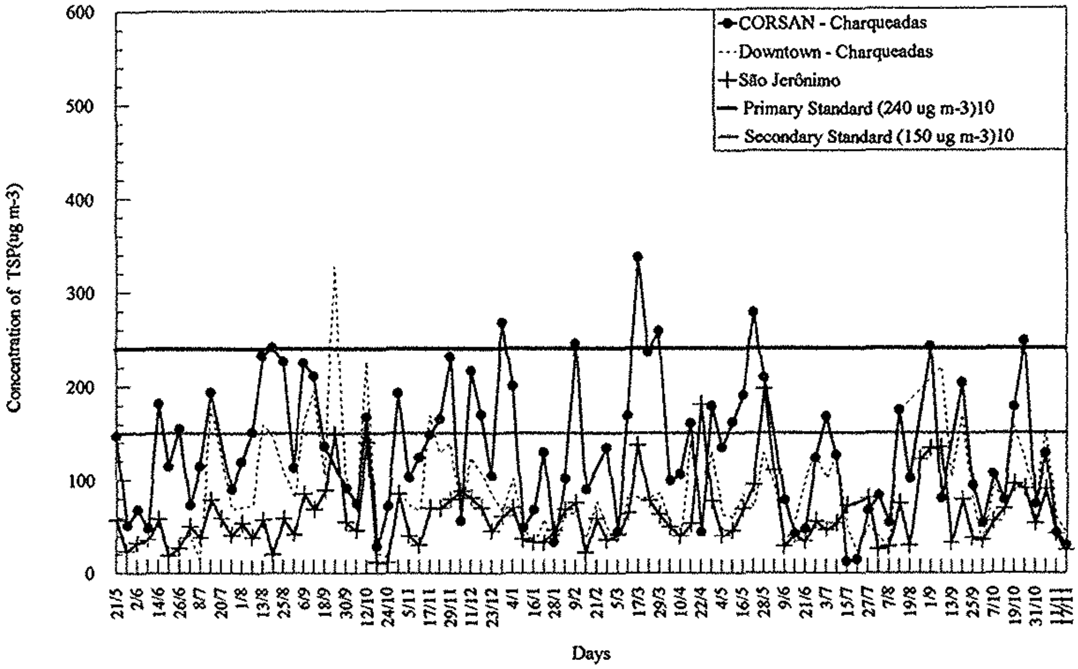


Figure 4. Concentration of total suspended particles –TSP ($\mu g\ m^{-3}$) determined during the period of May 1994 to November 1995 for the three sampling stations in of Charqueadas and São Jerônimo.

Table 1 also shows a comparison of our experimental results and those of another urban center, Rio de Janeiro, Brazil. As can be seen, Fe and Mn are present in higher concentrations in Charqueadas and São Jerônimo, indicating atmospheric contamination due to the siderurgic industry. On the other hand, the concentrations of Pb were lower, also when compared to standards recommended by several countries (0,3-2,0 $\mu g\ m^{-3}$)[12].

Table 1. Environmental concentrations of metals associated with total suspended particles in Charqueadas and São Jerônimo Municipalities compared to Rio de Janeiro.

	Charqueadas						São Jerônimo			Rio de Janeiro
	CORSAN($\mu g\ m^{-3}$)			Downtown($\mu g\ m^{-3}$)			São Jerônimo($\mu g\ m^{-3}$)			Average concentration in urban center * ($ng/\ m^3$)
	Mean	Max	Min.	Mean	Max.	Min	Mean	Max	Min.	Mean *
Fe	15,0	64,4	1,51	6,05	33,3	0,78	2,0	6,26	0,30	1231/2467 **
Mn	0,32	1,4	0,025	0,16	0,80	0,015	0,036	0,22	0,002	92
Cu	0,18	0,44	0,065	0,104	0,27	0,048	0,098	0,18	0,48	155
Pb	0,14	1,2	0,019	0,095	0,87	0,0016	0,052	0,119	0,004	715
Cr	0,14	1,02	0,015	0,063	1,14	0,005	0,022	0,086	0,002	60
Ni	0,08	0,85	0,003	0,027	1,36	0,0015	0,018	0,134	0,003	52
Co	0,0084	0,04	0,0009	0,007	0,13	0,0008	0,006	0,043	0,0010	39
Cd	0,0065	0,15	0,0011	0,005	0,013	0,0009	0,004	0,008	0,0007	5,2
PTS	162	499	29,4	98,97	328	32,24	61,01	197,0	19,2	--

Sources : * Mean environmental concentration in urban locations [14]

** Mean environmental concentration in an urban center, Rio de Janeiro, Brazil [15]

This was to be expected, since lead has not been used as a gasoline additive (as tetraethyl lead) since 1988, and was the principal source of pollution in urban atmosphere.

Table 2 presents Pearson's correlation coefficient for the concentrations of metals, total suspended particles and weather conditions for the three station. Most elements studied showed a higher correlation coefficient for the two station in the town of Charqueadas. For Fe/Mn and Mn/Cr correlation coefficients were also high for the sampling station in São Jerônimo.

Table 2. *Pearson's correlation coefficient for the concentration of metals, total suspended particles and weather data for the three stations.*

	Fe	Mn	Cu	Pb	Cr	Ni	Co	Cd	PTS
CORSAN - Charqueadas									
Fe	1,000	0,7372***	0,7583***	0,7349***	0,7356***	0,4449*	-0,2820	-0,1284	0,1737
Mn		1,000	0,6851***	0,7628***	0,7397***	0,5919**	-0,1193	-0,0762	0,0975
Cu			1,000	0,6519**	0,7149***	0,4359*	-0,3118	-0,0504	0,0239
Pb				1,000	0,8507***	0,4918*	-0,1534	-0,0939	0,0487
Cr					1,000	0,7574***	-0,1021	-0,0580	0,1609
Ni						1,000	0,1642	-0,0215	0,0551
Co							1,000	-0,1108	0,1019
Cd								1,000	-0,1748
PTS									1,000
Downtown - Charqueadas									
Fe	1,000	0,7470***	0,7086***	0,8158***	0,5416*	0,2938*	-0,1134	0,5014*	0,4866*
Mn		1,000	0,5762**	0,6961***	0,6571**	0,4773*	-0,1462	0,2863	0,3744
Cu			1,000	0,5169*	0,7776***	0,5942**	-0,1796	0,5200*	0,4304*
Pb				1,000	0,4133*	0,1059	-0,1007	0,5876**	0,2112
Cr					1,000	**0,9094***	-0,0213	0,5280*	0,3221*
Ni						1,000	-0,0712	0,3251	0,2613
Co							1,000	-0,1458	-0,1281
Cd								1,000	0,0775
PTS									1,000
São Jerônimo									
Fe	1,000	**0,6828*****	0,2959*	0,2490	0,4998*	0,2228	-0,1796	-0,0297	0,2911*
Mn		1,000	0,5274*	0,3201*	**0,8571*****	-0,0270	-0,2496	0,2367	0,2164
Cu			1,000	0,2948	0,5341*	-0,1942	-0,2904	0,1668	-0,0989
Pb				1,000	0,3281*	0,0698	-0,059	0,2719	-0,0994
Cr					1,000	0,0420	-0,2980	0,1776	0,1523
Ni						1,000	-0,1768	-0,3038	-0,0589
Co							1,000	**0,7349*****	-0,2118
Cd								1,000	0,2350
PTS									1,000

** Significance factor at 0,1 % ** Significance factor at 1 % * Significance factor at 5 %

These results, associated with the preferential wind direction (E-SE) suggest that the steel plant is responsible for the emission of these elements. Its already mentioned, this plant dues not have any control system for particulate matter[13].On the other hand, Pb is, probably due to the coal-fired power station located nearby. This power station is also partially responsible for emissions of Cu and Ni. These elements together with Pb are concentrated at the surface of finer ash particles and are hard to retain by the electrostatic precipitator.

The differences determined for metals from one sampling site to another may be attributed to their association to different types of particles (probably finer ones) that reach more distant sites from the emitting sources.

Figures 5 to 13 illustrate the annual geometric means for metals for the period from May 1994 to November 1995. A difference in the spacial distribution of Fe, Mn, Cr and Ni, whose concentrations were higher at the Corsan station was verified. The other elements did not show any significant difference, presenting practically the same behavior at the three sites studied.

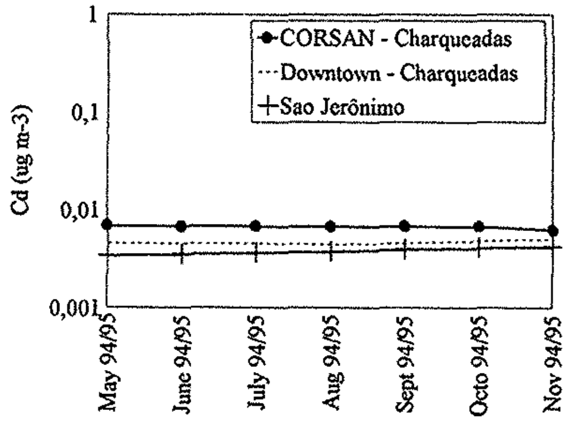


Figure 5. Annual geometric mean for Cd ($\mu g\ m^{-3}$)

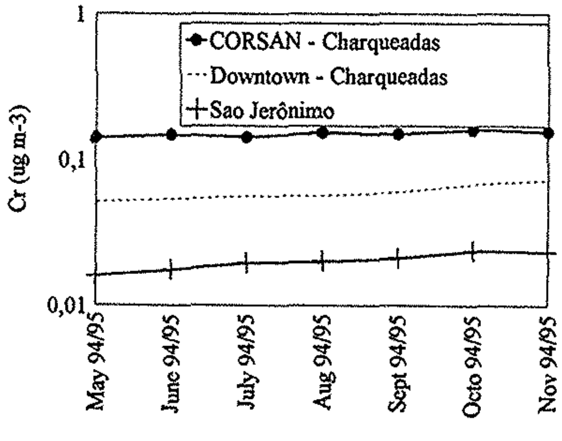


Figure 6. Annual geometric mean for Cr ($\mu g\ m^{-3}$)

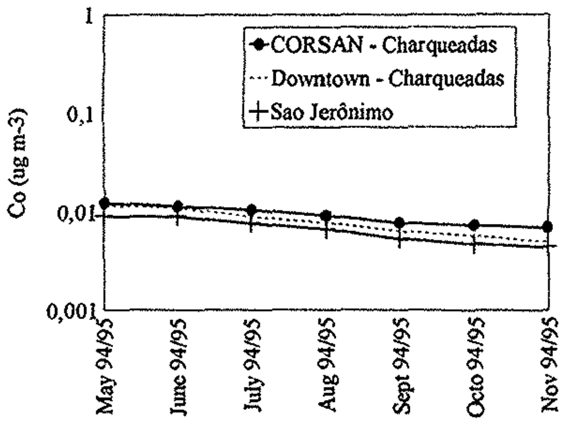


Figure 7. Annual geometric mean for Co (μg m^{-3})

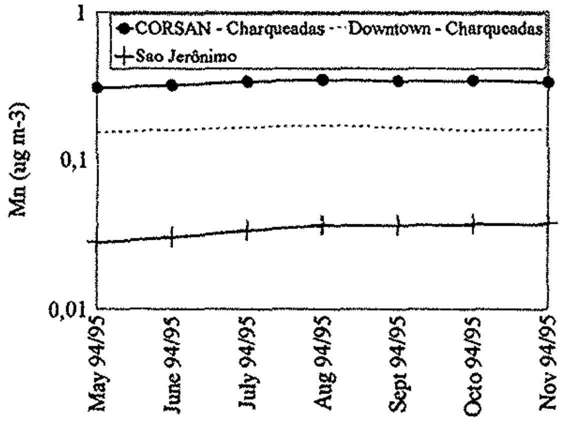


Figure 8. Annual geometric mean for Mn (μg m^{-3})

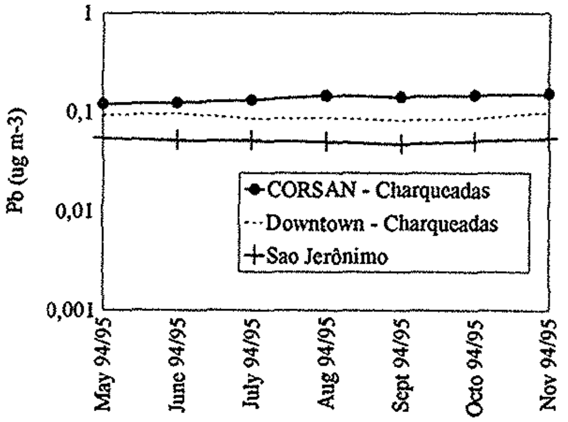


Figure 9. Annual geometric mean for Pb (μg m^{-3})

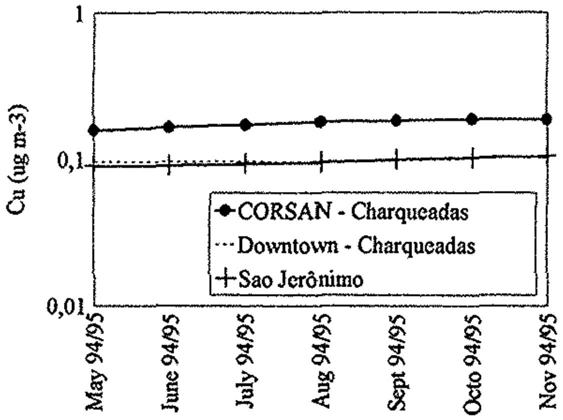


Figure 10. Annual geometric mean for Cu ($\mu g\ m^{-3}$)

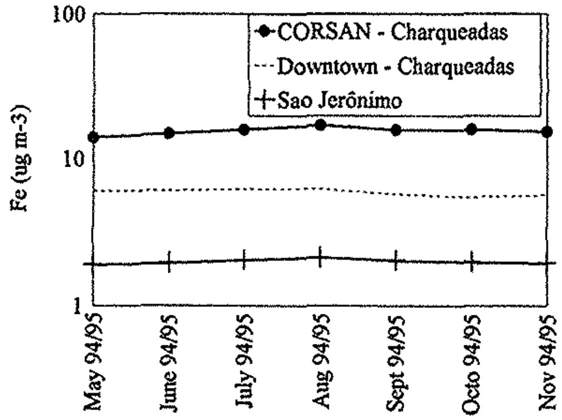


Figure 11. Annual geometric mean for Fe ($\mu g\ m^{-3}$)

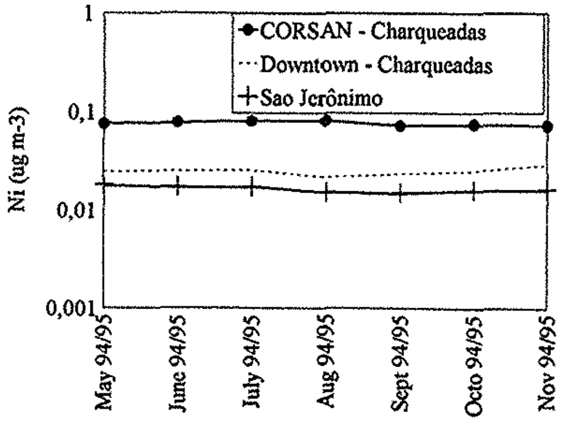


Figure 12. Annual geometric mean for Ni ($\mu g\ m^{-3}$)

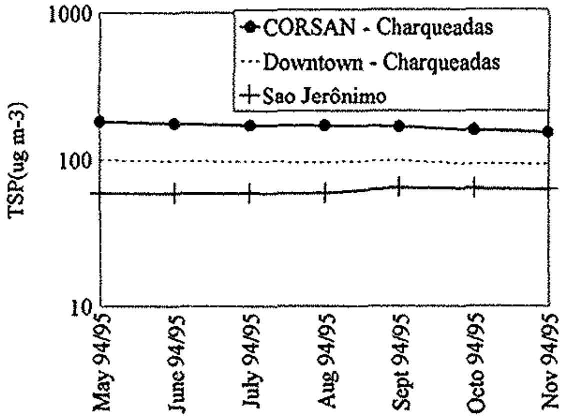


Figure 13. Annual geometric mean for TSP(μg m^{-3})

CONCLUSIONS

The experimental results obtained for the period of May 1994 to November 1995 for the three stations studied (Corsan and Downtown Charqueadas and São Jerônimo) showed that according to Brazilian and German standards, the air quality is not affected by SO_2 and NO_2. On the other hand, the municipality of Charqueadas showed contamination by total suspended particles, both primary (240 μg m^{-3}) and secondary (150 μg m^{-3}) Brazilian standards being surpassed by several orders. Metals associated to total suspended particles indicated elevated environmental concentrations of Fe due to local anthropogenic sources. Fe along with Mn, Cu, Cr and Ni are probably originate from of the local siderurgic industry that does not use any controlling systems for particulates. The presence of Pb and part of Cu and Ni can be attributed to the coal-fired power station, located near the siderurgic industry. Apparently, the efficiency of the particle retaining systems employed decreases for finer particle size (< 10 μm). The best correlation for the elements was obtained for the CORSAN station for Mn/Fe, Cu/Fe, Pb/Mn, Cr/Ni, Cr/Cu, Cr/Mn and Cr/Fe. For the Downtown Charqueadas sampling site the best correlation was obtained for Cr/Ni, Cr/Cu and Pb/Fe. These results suggest, that there exist associations of these elements to particles of different types and sizes, for the case of total suspended matter.

ACKNOWLEDGMENTS

We are thankfull to Programa de Apoio Desenvolvimento Ciência e Tecnologia / Geociência e Tecnologia Mineral(PADCT/GTM) for financial support . Special thanks is also given to ELETROSUL for technical support.

REFERENCES

1. M. Pires; H. Fiedler and E.C. Teixeira, *FUEL, 76, (14/15),* 1425-1437 (1997).
2. M. Pires and E.C.Teixeira *FUEL,71,*1093-1096 (1992).
3. E.C.Teixeira, J.C. Samama and A. Brun., *Environmental Technology.* 13, 10, 995-1000 (1992).
4. I.M. Schmidt, "Trace Elements from Coal Combustion Emissions", IEA CR/01 London, IEA Coal Research, p.87,1987.
5. P.P. Andrade. *Estudos dos efeitos da poluição ambiental área sobre a saúde da população entre duas cidades da região Carbonífera do Rio Grande do Sul,* Dissertação de Mestrado, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil, p.104, 1989.
6. ASTM - American Society for Testing and Materials, *"Standard Test for Sulfur Dioxide Content of the Atmosphere(West-Gaeke Method): D - 2914"* ,West Conshohocken, PA, Vol. 11.03, 1995.
7. USEPA. United States Environmental Protection Agency. "*Equivalent Method for the Determination of Nitrogen Dioxide in the Atmosphere (Sodium Arsenite Method).*" Quality Assurance Handbook of Air Pollution Measurements Systems Ambient Air Specific Methods. Section 2.4,Vol.II, 1981.
8. USEPA - United States Environmental Protection Agency. "*Quality Assurance Handbook for Air Pollution Measurements System, Ambient Air Specific Methods.*" Vol. I and II, 1987.
9. J.C.D. Sanchez, E.C. Teixeira, T. Isaia, G. Vecchio, M.H.D, Pestana & M.L.L. Formoso, M.L.L. *Estudo de partículas totais em suspensão e metais associados na região do Baixo Jacuí, R.S.* In: V Congresso Brasileiro de Geoquímica e III Congresso de Geoquímica dos Países de Língua Portuguesa, Niterói, RJ, Brazil, Proceedings...5p., 1995.
10. CONAMA. - Conselho Nacional do Meio Ambiente. Resoluções, CONAMA 1984-1991,4ed., p.245, Brasília, Brazil, 1992.
11. JICA/ELETROSUL/CEEE-Japan International Cooperation Agency/Centrais Elétricas do Sul do Brasil.AS./Companhia Estadual de Energia Elétrica-RS. "*The Study on Evaluation on Environmental Quality in Regions under Influence of Coal Steam Power Plants in the Federate Republic of Brazil.*" Final Report, 1997.
12. CETESB - Companhia de Tecnologia de Saneamento Ambiental, *Compilação de padrões ambientais.* São Paulo, SP, Brazil,1990.
13. FEPAM- Fundação Estadual de Proteção Ambiental. Processo, "*Projeto de controle das emissões atmosféricas da Aços Finos Piratini*", Porto Alegre, RS, Brazil,1996.
14. Nriagu, J.O. *Environment. 32, (7),* 1-33 ,1990.
15. H.A.Trindade, W.C. Pfeiffer, H. Londres and C. Costa Ribeiro, *Envir. Science Techn.15, (1),* 84-89 (1981)

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, N° 6, 1998

COMPARATIVE STUDY OF THE CHEMILUMINESCENCE PRODUCED BY THE ACTIVATED POLYMORPHONUCLEAR LEUKOCYTES IN PHYSIOLOGICAL AND VARIOUS PATHOLOGICAL CONDITIONS

R. M. OLINESCU[#], MARIA GREABU[##], D. CROCNAN[##], F. A. KUMMEROW[#], VALY CONSTANTINESCU[###], FRAGA PAVELIU[##]

[#] The Burnsides Research Laboratory, University of Illinois, Urbana, ILL 61801, USA
[##] Department of Dentistry, University of Medicine 'Carol Davila', Bucharest, Romania
[###] National Institute of Hygiene, Bucharest, Romania.

ABSTRACT

The chemiluminescent emission released by activated polymorphonuclear leukocytes has been known for a long time, but its clinical use is still scarce. We suggest the as a quantitative measurement of chemiluminescence the stimulatory index (ratio of the chemiluminescence value of stimulated polymorphonuclear leukocytes, to non-stimulated leukocytes) obtained for the same individual. The results obtained by a standardised simplified technique for more than 2000 individuals (healthy persons such as medical personnel, athletes, soldier and patients suffering from cardiovascular disease, cancer and pneumoconiosis) explain the still restricted use of chemiluminescence. There was a wide range of individual variations and an overlap of normal physiological and pathological values. A significant statistical difference was obtained only for patients in the acute phase of the disease. The chemiluminescence measurement of phagocytic activity of leukocytes is strongly influenced by age, diet, presence of stress and chronic inflammations.

RESUMO

A emissão de quimiluminescência por leucócitos polimorfonucleares ativados é conhecida já faz muito tempo, porém as suas apilcações clinicas estão muito escassas. Este trabalho propõe como medida de quimiluminescência o índice estimulatório (razão do valor da quimiluminescência de leucócitos polimorfonucleares estimulados e não-estimulados) para um mesmo indivíduo. Resultados experimentais obtidos para mais de 2000 pessoas (alguns gozando de boa saúde como atletas. soldados, componentes do corpo médico e pacientes sofrendo de doenças cardiovasculares, câncer e pneumoconiose explicam o uso ainda restrito da quimiluminescência. Para um número grande de indivíduos aconteceu uma superposição de valores normais e patológicos. Uma diferença estatisticamente significativa foi observada somente no caso de pacientes na fase aguda da doença. A medida de atividade fagocítica de leucócitos usando quimiluminescência é altamente influenciada pela idade, dieta, presença de estresse e inflamações crônicas.

KEY WORDS: chemiluminescence, phagocytosis, leukocytes.

DOI: 10.48141/SBJCHEM.v6.n6.1998.27_1998.pdf

INTRODUCTION

The phagocytic activation of oxidative metabolic pathways of polymorphonuclear leukocytes (PMNL) has been shown to yield electronically excited molecules and free radicals. These reactive oxygen species (ROS), either by themselves or by interaction with cellularcomponents, produce a long lasting emission of chemiluminescence (CL) [2, 3, 4]. In spite of the fact that Allen discovered the CL produced by activated PMNL in 1972 [1], its clinical utilisation is sill scarce [7, 16]. The lack of an internationally accepted standardisation of the procedure, the final expression of the result of the determination, use of various instrumental techniques, interference with ingested antioxidants or drugs and the wide range of individual values might explain the limited utilisation of CL for clinical purposes.

Depending on the particular requirements [8, 21] of an assay system whole [20], purified PMNL [1, 2, 3, 4, 7], alveolar macrophages [17], or natural killer cells [10] were used as a source of CL. The in vitro activation of the phagocytic cells was triggered by various stimuli such as: opsonized zymosan [1, 2, 3, 4, 7], or bacteria [18], phorbol myrimethionyl-leucyl-phenylalanine [6].

In previous studies [14, 16], we showed that the CL emission of human activated PMNLs in healthy individuals depends also on age and the presence of physical or psychical stress. We nowl propose a simplified procedure for the measurement of the CL emission of PMNL in order to make its use more convenient for large clinical scale utilisation.

MATERIAL AND METHODS

The study was performed on 200 healthy individuals, aged 20-70 years, of both sexes and varied occupations. These subjects had normal haematological patterns, including the total leukocyte count.

The study also included 1800 patients, mostly (1100) cardiac catheterised patients from Carle Hospital, Urbana USA, pneumoconiosis (300) and lung cancer (400) from clinics of occupational diseases and of Radiobiology, Fundeni Clinical Hospital, Bucharest, Romania.

The suspension of purified PMNL was obtained by using the two step Histopaque kit (Sigma Chemical Co. St. Louis, USA, No.1077). The final dilution of PMNL to 1 x 10^7 cells/ml was performed by using Hanks' balanced salt medium (Gibco Life Technol. grand Bland, New York).

We also used a simplified procedure: ten ml whole blood containing 10 units of heparin was centrifuged at 700 G for 10 minutes. The supernatant containing the plasma was discarded, and its volume was replaced with a cold solution of ammonium chloride 0.87 %. After thorough mixing, the whole hemolysate was centrifuged for 7 minutes at 700 G. This procedure was repeated and centrifuged for 5 minutes at the same speed. The colourless residue that contained only leukocytes was washed with Hanks' solution. Finally, a suspension of 1 x 10^7 cells/ml was obtained by using Hanks' solution for dilution.

For both procedures, the final suspension contained neutrophils, 90% for the first and 70% for the second. For both procedures the blue tripan exclusion test showed approx. 98% viable cells.

The determination of phagocytic capacity of purified PMNL consists in the following procedure: For each individual, two samples are used. In each of the tubes 100 μl leukocyte suspension (1 x 10^6 cells/ml) and 100 μl luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) 0.1 mmol were introduced. In the first tube, nonstimulated, 800 μl of Hanhs' solution was added while in the second, stimulated only 700 μl of Hanks' was added. Both samples are kept for 10 minutes at 37°C. Then, 100 μl opsonized zymosan 1 mg/ml was added only in the stimulated sample. Both samples were introduced in the counter or luminometer and the emission of CL was recorded for 30-60 minutes. The identical technique was used for both procedures. In healthy persons, the lymphocytes which account for approx. 20 % of total leukocytes do not produce CL under such conditions, thus are not interfering with the determination.

Zymosan was prepared by boiling fresh yeast in alkaline medium in the conditions described by the LKB-Wallac (application procedure Nos 513) and was opsonized afterwards with AB serum. The final suspension was adjusted to 10 mg/ml and was divided into portions of 1 ml and kept at -20 °C until utilisation.

A Beckman beta Scintillation Counter LS-3801 with special single photon monitor equipment was used for measuring the CL emission. The final result for both procedures was expressed as the stimulatory index (SI) of phagocytosis obtained from the ratio of the CL value at any time of the stimulated sample and the CL value from the same period of time of the nonstimulated sample. Thus for each individual, both procedures included two samples, both non-stimulated and stimulated and the ratio of the measurement for the same period of time provided the SI.

All data were transformed to logarithmic scale in order to fit a Gaussian pattern. The calculations were performed using a statistical package from BMDP Statistical Software Inc. The significance of the differences between each value presented by two groups was evaluated by the Student's t test with $\rho < 0.05$, considered statistically significant.

RESULTS

Comparison of the procedures for obtaining PMNL

The viability of PMNL is essential in order to obtain a reliable measurement of the CL emission. Therefore, the purification of PMNL should not be of long duration to harm the cells. This explains why the testing of viability of purified PMNL by trypan blue exclusion is so important.

As can be seen in Fig. 1, the difference between the known procedure and the simplified variant we proposed is clear-cut. The known procedure is based on a suspension of PMNL, where neutrophils are 90 % of the total count, while for the second procedure, these cells account only for 70 % for a healthy person. This explains why for the same number of cells (1 × 10^6 cells/ml), the first procedure yielded a higher CL. For

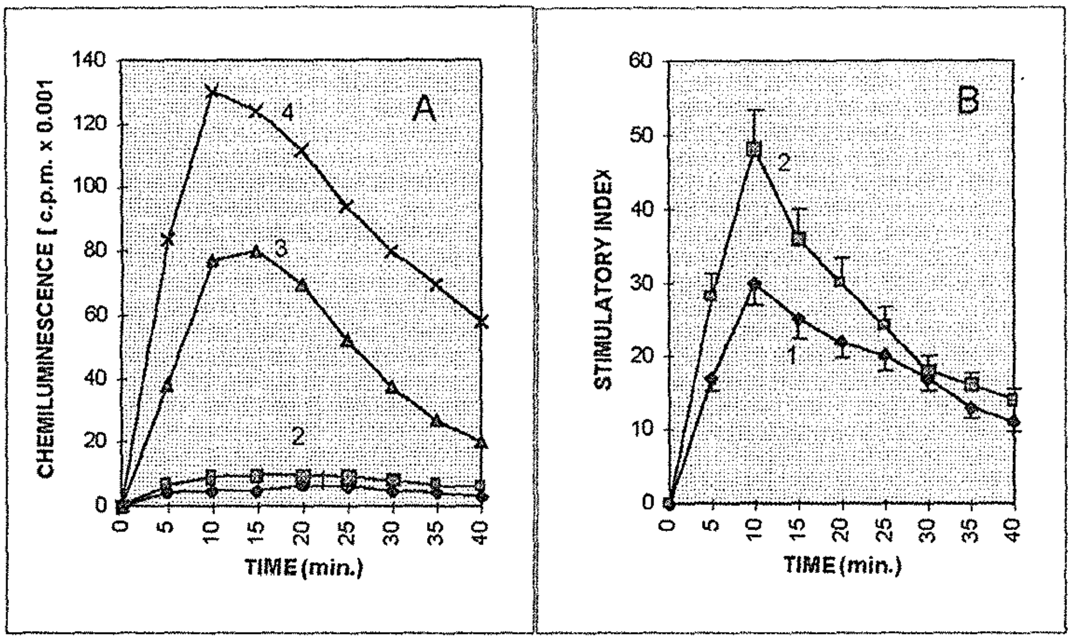


Fig. 1. - The kinetics of chemiluminescence produced by purified polymorphonuclear leukocytes.

A. The pattern of chemiluminescence mesurement for (2), non stimulated in the first procedure, and (1) in the second procedure, and stimulated in the first (4) and the second (3) procedure.

B. B The course development of the stimulatory index of phagocytosis for the second (1) and for the first (2) procedure.

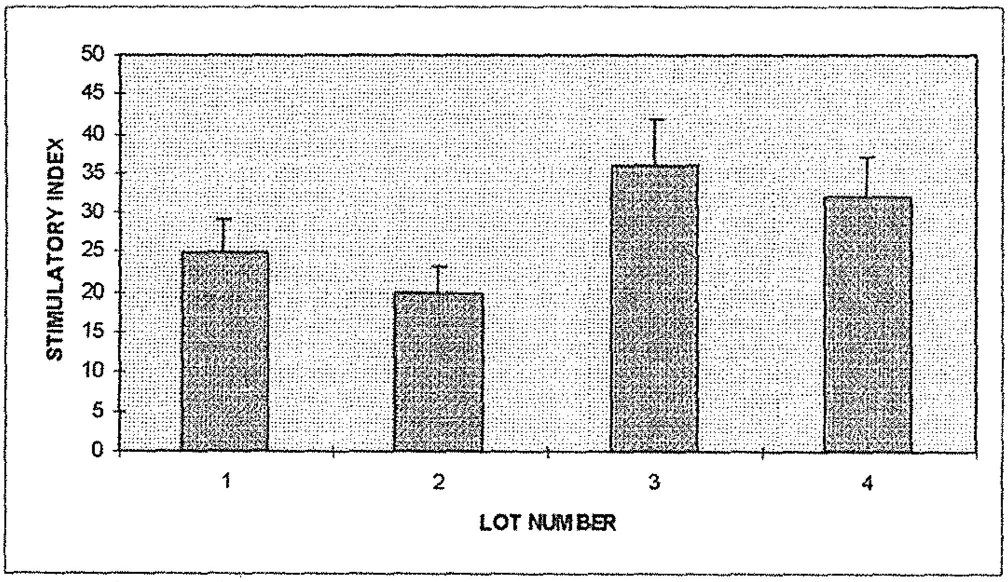


Fig.2 . - The variation range of the stimulatory index of polymorphonuclear leukocytes for healthy individuals based on measurement of the chemiluminescence emission according to the simplified procedure. The whole lot of healthy individuals consisted of four groups of 50 as follows: 1. Athlets (swimmers and bicycle runners), 2. Soldiers (18-20 years old), 3. Old persons (60-80 years), 4. Medical staff (medical doctors and nurses).

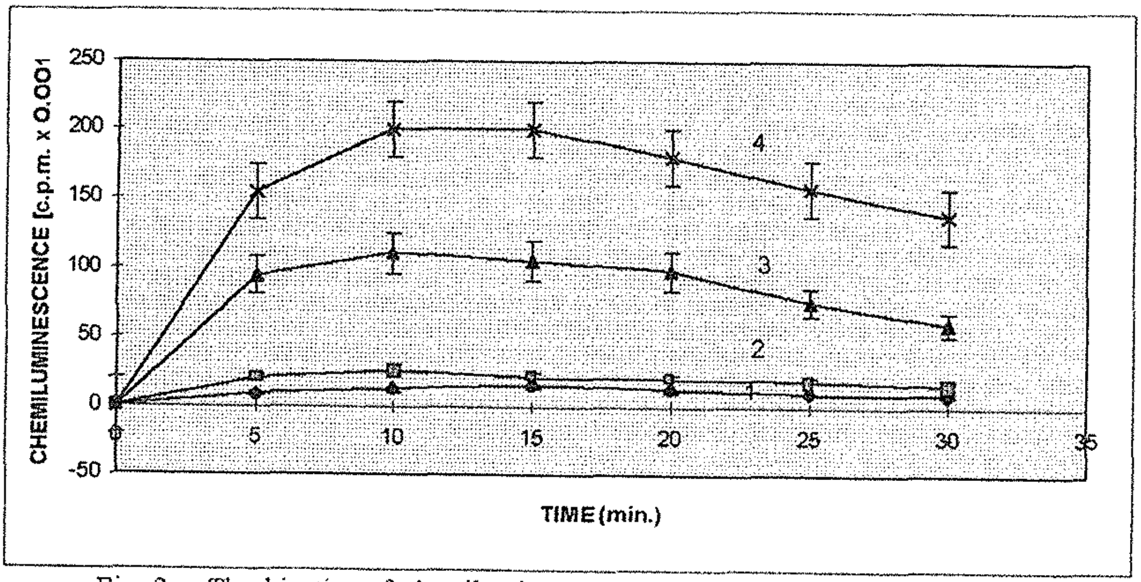


Fig. 3. - The kinetics of chemiluminescence measurement of phagocytosis in patients with pneumoconiosis.

Physiological range includes for normal individuals. (1) Non-stimulated and (3) stimulated values,

Patients with pneumoconiosis, (2) Non-stimulated and (4) stimulated samples.

The mean standard error is the result of measurements performed on 200 healthy individuals and 300 patients with pneumoconiosis.

TABLE 1 The variations of the stimulatory index (SI) of phagocytosis in some pathological conditions

CONDITION		NUMBER OF PATIENTS	STIMULATORY INDEX	SIGNIFICANCE $\rho<$
CONTROL		200	25 ± 7	
PNEUMOCONIOSIS		300	64 ± 14	0.01
LUNG CANCER		400	43 ± 18	0.08
CARDIAC CATHETERISED PATIENTS	**0 % stenosis**	340	53 ± 12	0.05
	80 - 100 % stenosis	760	61 ±17	0.01

nonstimulated samples, the two procedures provide no significant difference. As seen in Fig. 1B, where the CL measurement is expressed as the SI (stimularory index) the difference between procedures is smaller and statistically non significant. The first procedure is more time consuming and this makes it less attractive for a wide range of utilisation.

Physiological range of stimulatory index

The stimulatory index of phagocytosis is influenced by any chronic inflammation or stress condition. As presented in Fig. 2 in a whole lot of healthy individuals, the SI differs according to age, being significantly higher to older persons as compared with younger ones (athletes or soldiers).

The second observation is related to the occupational status of individuals. The medical staff, that include medical doctors and nurses, exhibits a higher statistically significant phagocytosis as compared with the athletes and soldiers groups. The variance of the individual values is also higher in the last group as compared with the others. The smallest variance was noticed for the soldiers group, which was the most homogeneous as compared with others, especially with the first one.

The determination of the stimulatory index in pathological conditions

Congenital deficiences of leukocytes, such as chronic granulomatosis disease (lack of respiratory burst during phagocytosis) or myeloperoxidase deficiency are the most widely known pathological conditions, where no CL emission is produced upon in vitro activation [7, 21]. But these diseases are rare, so CL utilisation is scarce.

Pneumoconiosis, known as inflammation of respiratory pathways and the lungs arises mostly following occupational exposure to mineral dust or asbestos.

As seen in Fig. 3, in patients with different forms of pneumoconiosis (asthma, silicosis), a significant increase of CL emission was observed. While the CL emission of nonstimulated samples might be overlapping with the physiological range, for the stimulated samples, the increased values are statistically different as compared with the healthy persons. For a significant number of patients investigated, the difference is clear cut only in the acute period of the disease.

The determination of CL emission was performed before treatment in order to avoid the strong influence of drugs.

As presented in Table 1, we extended our study on several groups of patients. In all pathological conditions, the SI was increased, but over a wide range. In pneumoconiosis, the data were found significantly increaseed as was the case for the patients with 100% stenosis.

For the patients with lung cancer, a wide range of modifications were noticed, but in most cases the individual variations were so high, that no statistical interpretation was possible. Similar wide ranges of modifications were noticed for patients with 0% stenosis, where the presence of acute inflammations might explain the chest pain, as well as the higher value of SI.

DISCUSSION

The obtention of data presented in our study performed on a large population of 2000 individuals was possible only by using a simplified procedure for purifying the PMNL. As shown in Fig. 1, our simplified procedure is simple, not expensive and reliable may be used for a large number of individuals.

As shown in Fig. 2, the data for healthy individuals are greatly influenced by many factors related to age, occupation and exposure to pathogens (medical staff) or stressful conditions (athletes, medical staff). The presence of chronic inflammatory ailments could not be ignored, especially for aged people or those exposed to pathogens (medical staff), mineral dust (miners, workers). Such observation may be extended to stressed people or with non defined pain as those with 0% stenosis.

For individuals with higher levels of phagocytosis, the increased levels of the SI suggest a non specific parameter with a strong individual character. As shown in Fig. 3 and Table 1 the analysis of the data for a lot of patients did not show its clinical value. The CL measurement of phagocytosis should be performed before treatment and as it possesses an individual trait. The variation of SI might offer the possibility to monitor the efficiency of the treatment and to evaluate the course of inflammations, which very often are present in a wide range of pathological conditions.

Such interpretation focused on individual level and the monitoring of the evolutive course of the disease and treatment is superior to the previous clinical interpretations [5, 7, 9, 11, 12, 13, 15, 19]. According to our data, the CL measurement of phagocytosis is related with the acute phase of diseases [22], as well as their chronic evolution. In almost all cases, smoking (present or within last 5 years) significantly increased the CL measurement. The SI is a dynamic parameter that mirrors the response of the phagocytic activity of leukocytes to various endogenous situations.

REFERENCES

[1] **R. C., Allen, R. L. Strjenholm, H. L. Steel,** *Biochem. Biophys. Res. Comm,.* 47, 680 - 687, (1973).

[2] **R.C., Allen,** in "Bioluminescence and chemiluminescence", I., Schölmerich, R. Anderson, W.G. Wood, Eds., John. Wiley and Sons, Chichester and New York, 1987, pp. 13 - 22.

[3] **B.R., Anderson, A.M. Brendyel, F. Blintt,** *Infect. Immunol.*, 17, 62 - 68, (1977).

[4] **I., Arnhold, S. Mueller, K. Sonntag,** *J. Biolum. Chemilum.*, 8, 307 - 313,)1993).

[5] **F., Banaba Allah, A. Gargani,** *Pathol. Biol.*, 44, 705 - 711, (1996).

[6] **C., Dahlgreen,** *J. Biolum. Chemilum.*, 6, 29 - 35, (1991).

[7] **P., De Sole,** *J Biolum. Chemolum.*, , 4, 251 - 262, (1989).

[8] **A., Farinelli, M. Seti, F. Puppo,** *APMIS,* , **101**, 500 - 509, (1996).

[9] **M. I., Furman, R.C. Becker, I. Savagean,** *Am. J. Cardiol,* 78, 1945 - 952, (1996).

[10] **S. L., Helfand, I. Werkmaister, I. C. Roder,.** *J. Exp. Med.*, , **43**, 744 - 752, (1982).

[11] **M., Holme, P. Maasilta, M. Ristola,** *Int. J. Radiat. Oncol.,* 1995, **31**, 93 - 101

[12] **K., Ley,** *Cardiovasc Res.,* **32**, 733 - 743, (1996).

[13] **W. K. C., Morgan,** in "Cool workers pneumoconioses in occupational lung diseases" W. K. C. Morgan, A. S. Seaton, Eds., Saunders, Philadelphia, 1994, pp. 665 - 676.

[14] **R. M., Olinescu, V. Radaceanu, Stela Nita,** *Rev. Roum. Med. Medicine Int.*, **30**, 201 - 207, (1992).

[15] **R. M., Olinescu, F. A. Kumerrow, B. L. Handler,** Age and Aging, accepted for publication, (1996).

[16] **R. M., Olinescu, Stela Nita, D. Crocnan,** *Rev. Roum. Med. Int.,* **31**, 109 - 118, (1993).

[17] **M. J., Parnham, C. Bittner, J. Winklemann,** *Agent and Actions,* **21**, 617 - 621, (1991).

[18] **P., Robinson, D. Wakefild, R. Penny,** , *Infection Immunity,* **43**, 744- -752, (1982).

[19] **L., Schrod, E. Honfmann, H.B. Stockenhousen,** *Acta Paediatr.,* **85**, 719 - 725, (1996).

[20] **R. J., Selvaraj, A. J. Sbarra, C. L. Cetrullo, G. W. Mitchell,** *J. Reticuloendothelial Soc.,* , **31**, 3-16, (1982).

[21] **M. A., Trush, M. E. Wilson, K. Van Dyke,** in *"Methods in Enzymology",* vol. **57**, S. P. Colowick and N. O. Kaplan, Eds., Academic Press, New York, 1978, pp. 462 - 494

[22] **G., Uras, F. Carballo,** *Gut,* **39**, 40 - 44, (1996).

The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM.
http://www.sbjchem.com.
This text was introduced in this file in 2021 for compliance reasons.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, N° 6, 1998

COMPARATIVE STUDY OF BIOSORPTION OF METALLIC CATIONS BY DIFFERENT BACTERIA

T. Gavriloaiei*, Raluca Mocanu, Maria Calistru***, R. Olariu****

* University "Al.I.Cuza" Iasi, Faculty of Geography-Geology, 20A Calea Copou, 6600 Iasi, Romania, e-mail: tgavrilo@vela.uaic.ro
** University "Al.I.Cuza" Iasi, Faculty of Chemistry, 71B Bd. Mangeron, 6600 Iasi, Romania
*** Agency of Environmental Protection, 10 Vascauteanu, 6600 Iasi, Romania

ABSTRACT

Certain species of microorganisms have been found to accumulate surprisingly large quantities of important metals, involved in the toxicity provoked by human activities (Cd, Pb, Hg) and metals of economic values (Ag, Au). Microbiological methods are applied to large-scale recovery or removal of metallic ions from aqueous solutions. These apllications involved the removal of heavy metals from sewage sludge, industrial effluents and mine or waste waters. This process has been developed using immobilized extracellular or cellular ligands or more simple chemical models based upon them. The uptake of metal ions on the cell surface and their translocations into the cell are well known natural processes. These adsorption processes could be expressed using Langmuir isotherms. Fe^{2+} and Mn^{2+} appeared to be the most effective cations for adsorption by *Bacillus subtilis*, *Pseudomonas aeruginosa*, even by *Saccharomyces cerevisiae*, while the Zn^{2+} cation, in spite of a great value of maximum adsorption, has a toxic action on microorganisms and the "detoxification" mechanism depends on genetic control.

Key words: bioadsorption, bioaccumulation, bacterial species, Langmuir isotherm

RESUMO

Algumas espécies de microorganismos acumulam quantidades surpreendentes de metais envolvidos na toxicidade provocada por atividades humanas (Cd, Pb, Hg) e de outros importantes em termos de valor econômico (Ag,Au). O presente trabalho trata da remoção de metais pesados do esgoto, efluentes industriais e aguas residuárias provenientes de mineração o outros processos. Foi estudado o processo de bioacumulação de metais usando duas espécies de bactérias e uma levedura. O processo de adsorção foi descrito usando isotermas de Langmuir. A adsorção mais eficiente aconteceu para íons de Fe^{++} e Mn^{++} no caso das tres espécies estudadas, *Bacillus subtilis*, *Pseudomonas aeruginosa* e *Saccharomyces cerevisiae*. Por outro lado, o cátion de Zn^{++} que tem um alto valor de adsorção máxima, exibe um efeito toxico sobre os microorganismos e o seu mecanismo de "detoxificação" depende de controle genético.

DOI: 10.48141/SBJCHEM.v6.n6.1998.35_1998.pdf

INTRODUCTION

The processes of accumulation and uptake of heavy metals by microbial biomass are receiving increasing attention since the microbe-based technologies may provide an alternative to the recovery techniques of heavy metals from different materials (waste waters, low-grade ores etc.). Microbial cells (living or dead) and the products derived from their metabolism may be efficient bioaccumulators, both of the soluble and of the oxidized forms. At the same time, the groups with negative charge from the cell-wall components may ensure an efficient biosorptive system for metallic cations present in high concentrations in solutions.

The use of microorganisms in "leaching" processes for metal recovery from low-grade ores has received much importance in the last decades. The bacterial species involved in the biosolubilization processes are adapted to high concentrations of metallic cations; e.g. a strain of *Thiobacillus ferrooxidans* can be resistant to high concentrations of UO_2^{2+} (0.042 M), Cu (0.87 M), Ni (0.85-1.23 M), Zn (1.7 M) [1] or Al (0.37 M), Co (0.17 M), Mn (0.18 M) and Cr (0.1 M) [2].

The present study describes the bioaccumulation properties of two bacterial species (*Bacillus subtilis*, *Pseudomonas aeruginosa*) and one yeast (*Saccharomyces cerevisiae*) and the biosolubilization properties of *Bacillus megaterium*. The species (*B. subtilis*, *P. aeruginosa* and *S. cerevisiae*) have been obtained from the collection of the Department of Microbiology, "Al. I. Cuza" University, Iasi and *B. megaterium* has been isolated from soils by the authors.

B. subtilis, *P. aeruginosa* and *S. cerevisiae* proved to have a good adsorption capacity for metallic cations from their solutions, a fact which is known in the literature, while *B. megaterium* strain has been tested for the solubilization properties of metallic cations: Fe, Cu, Zn, Pb from copper concentrates, a phenomenon that has not been reported up to the present in the literature. The last aspect has been considered by us recently [3].

MATERIALS AND METHOD

In order to obtain young cultures, *B. subtilis* and *P. aeruginosa* strains have been inoculated on the usual culture media (i.e. broth), while the *S. cerevisiae* one - on the Sobourand medium [4]. After incubation at 37°C (48 h) for bacteria and 28°C (72 h) for yeast, respectively, the cultures have been developed on a special medium, to which the solution of cations subjected to analysis has been added, that means solutions of 0.2 $g.l^{-1}$ Fe^{2+} ($FeSO_4.7H_2O$), Mn^{2+} ($MnSO_4.4H_2O$) and Zn^{2+} ($ZnSO_4.7H_2O$). Subsequently, the samples were incubated at 37°C for bacteria and 28°C for yeast, respectively.

Bioadsorption of metallic cations has been tested in 250 ml Erlenmeyer flasks containing 40 ml culture medium, 10 ml bacterial inoculum and 50 ml solution from each cation subjected to analysis (Fe, Mn, Zn).

Small volumes of solutions have withdrawn every 24 hours, for a period of 6 days. The samples has been filtered and centrifuged, in order to eliminate the bacterial substratum and the supernatant solutions have been analyzed with an atomic absorption spectrophotometer of the Perkin Elmer 3300 type.

The adsorption capacity of metallic cations to the cell-wall surface of microorganisms can be expressed using the Langmuir isotherms in order to obtain the informations on "bioavalability" of active positions for metallic ions sites coordinations. The Langmuir isotherm may be written as follows [5]:

$$\frac{c}{\Gamma} = \frac{c}{\Gamma_{max}} + \frac{1}{k\Gamma_{max}} \qquad (1)$$

where c=is the concentration of adsorbed species at equilibrium, ($mg.l^{-1}$), Γ=is the amount of metallic ions adsorbed per unit of mass of adsorbent ($mg.g^{-1}$), Γ_{max}=is the maximum adsorption ($mg.g^{-1}$), k=the Langmuir constant related with the bonding energy.

The graphical expression of the (c/Γ) function at the equilibrium concentration (1/c) is correlated with the maximum adsorption (Γ_{max}) for each species.

RESULTS AND DISCUSSIONS

Analysing the adsorption capacities of the three cations by the *B. subtilis* species, it may be stressed that the Fe cation is the most adsorbed cation (almost 90% of the initial amount) a maximum being recorded in the 5th day of the process. The Mn cation is well adsorbed too by bacteria, with a maximum values of the adsorption process (82,3%) in the second day, while the Zn cation is "tolerated" by the bacteria. Because the adsorption of Zn^{2+} varied so little from a day to another, is demonstrating that the process take place until chemical equilibrium is attained between adsorption and desoption.

Figure 1 shows a plot of the Langmuir isotherm for the Fe cation adsorption by *B. subtilis*. The nature of the graph obtained for the different values of the equilibrium concentration, indicates that the process is adequate for a good adsorption (Γ_{max}=0.279), even at high concentrations of the analyzed cation. Usually, the solute amount adsorbed on the mass unit of adsorbant, increase in the same time with the metallic ion's amount, but not always in direct proportion. This thing obviously appeared from the graphical plot of the adsorption of Fe cation by *P. aeruginosa* (Fig. 2) (Γ_{max}=0.278), where the appearance of a sigmoidal curves corresponded to unfavourable adsorption at the highest Fe concentration [6].

The Fe adsorption process also occurs in good yields in the case of *S. cerevisiae* strain, as bioaccumulator (Γ_{max}=0.275) (Fig. 3). In the adsorption processes, *S. cerevisiae* is well known for its specificity for UO_2^{2+}: at higher temperatures and at pH values between 3.0 - 4.0, the cells accumulated about 15% of dry weight, but only 32% of cells showed the presence of "uranium dump" [7].

The main structural component of these bacterial walls, involved in bioaccumulation of these cations is peptidoplycan (a repeated dimer of N-acetylglucosamine and N-acetylmuranic acid, linked by a small peptide) [8,9]. This peptide contain rest of glutamic acid, whose carboxylate groups plays an important role in metal-binding. The capacity of *B. subtilis* to bind the metallic cations is

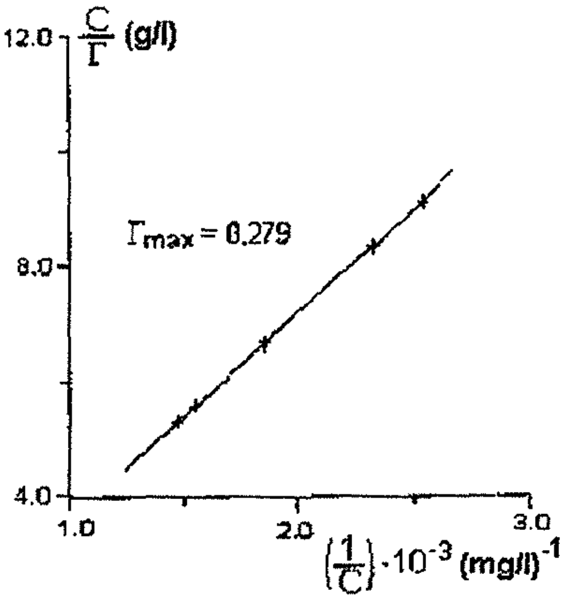


Fig. 1. Langmuir plot of ferrous sorption onto *B. subtilis*

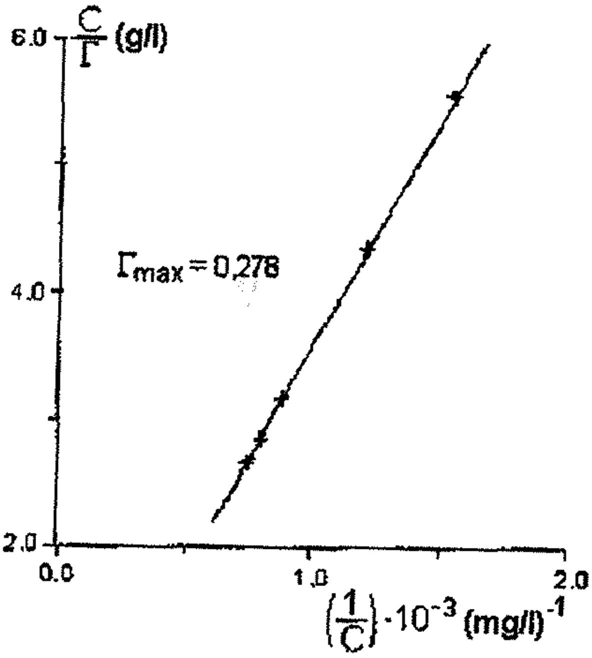


Fig. 2. Langmuir plot of ferrous sorption onto *P. aeruginosa*

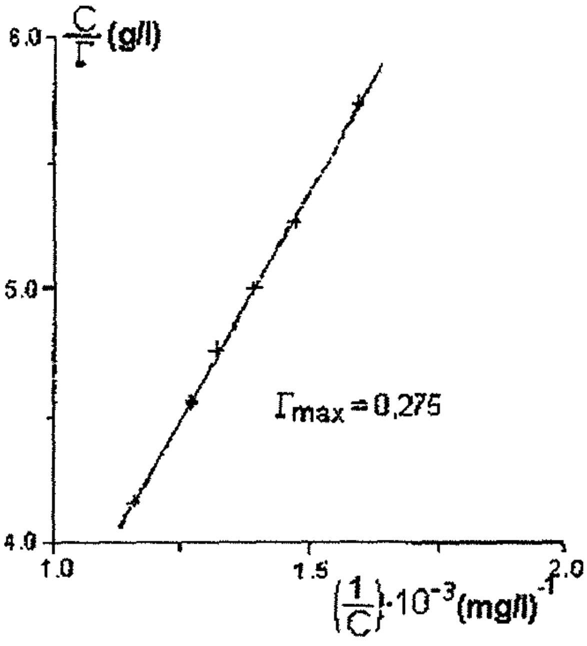


Fig. 3. Langmuir plot of ferrous sorption onto *S. cerevisiae*

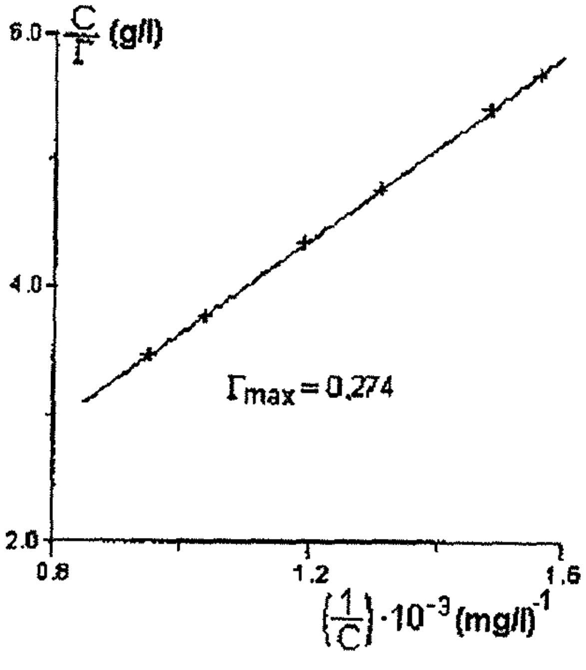


Fig. 4. Langmuir plot of manganese sorption onto *B. subtilis*

dramatically reduced, if the carboxylate group is esterified [10].

The peptidoglycan is followed by a second polymer, teichoic and/or teichuronic acid. These two compounds are linear polymers of glycerol phosphate and their contents in the cell-wall of *B. subtilis* is about 55% of dry weight [7]. Cell-walls of other Gram-positive organisms contain teichuronic acid, a carbohydrate made up of repeating units of a dissaccharide [7,10].

The anionic composition of the cell-walls might be varied function by the metallic cation's reactivity, which can substitute other metals. In this case, a competitivity for the occupancy of "active sites" from cellular walls structure is involved [8,9]. In Table 1 some classes of chemical compounds from the cell-wall composition of *B. subtillis* are given [11].

In Figures 4 to 6 the Langmuir isotherm for the adsorption processes of Mn by *B. subtilis, P. aeruginosa* and *S. cerevisiae*, respectively are presented. From the calculated values of Γ_{max} it results that both for *B. subtilis* and *P. aeruginosa*, the cation adsorptions by these two species, follow the same trends observed for the adsorption of Fe and Mn. So, the adsorption capacity of these two bacterian species are going on after a favourable mechanism, but there is no specificity for any one of the subjected cations. This thing could be explained based on the basis of the similar chemical's properties of these two cations (the stability in acidic medium, the tendency to form complex or hydratate compounds, close ionic rays, oxidability, medium strength after Pearson's theory), but could not be explained from the chemical composition point of view of cell-wall (Table 2).

Theoretically, it is possible that the metallic ions in high amounts to be intracellular accumulated, in spite of adsorption process to the cell-wall surface. Inside the cell, the cations could be precipitated as an oxalate or polyphosphate [10], but the transmembrane active transport for each cations is still unknown. An interesting example of intracellular accumulation is the metabolism-independent transport for uranium uptake by *P. aeruginosa* [7]. In this example, the uranium is taken up within 10 s and is localized into the cell, but only 44% of the cell, contained visible deposits.

The adsorption process of Mn by *S. cerevisiae* (Fig. 6) has developed with lower yields, Γ_{max}=0,279. In the first two days of determinations the process proceeds through the complexation of "active positions" from the cell-wall, after that the process develop through repeated sorption and desorption, until chemical equilibrium is attained.

The adsorption isotherm for the equilibrium distribution of a solute between the adsorbant and Zn solutions is shown in Figures 7 to 9. The values of Γmax are bigger than that obtained for the other two cations: 0.325, 0.324 and 0.329, respectively. This is not surprising because these values didn't show a more favourable adsorption compared with those for Fe and Mn cations. This cation (beside Cu) may be essential for microorganisms at small concentrations, while at high concentrations, he has a potentially action. The larger values for Γ_{max} for Zn adsorption processes are not determined by the ionic speciation, but may be explained by the "detoxification" processes of microorganisms. This process is not an usual one for microorganisms. It is coordinating by plasmides and is a manifestation of their resistance to different external stimuli. Many metallic ions are taken up by bacteria and are biotransformed in different non-toxic products [1,2,12].

Tab. 1. Chemical compiosition of *B. subtilis* cell-wall (11)

Amino-acids (g/100 g wall)		Hydrolysis products of teichoic acids	Monosaccharides present	Lipid contents (%)	Chemical composition
Lysine	6	Alanine			
Histidine	6	Glucose	Glucose		
Aspartic acid	1	Inorg. Phosphate	Galactose	0.7 - 3	%N %P $\%S_{red}$ 5.1 5.35 34.0
Glycine	5	Anhydroribitol	Manose		
Tyrosine	1.5	Ribitol			

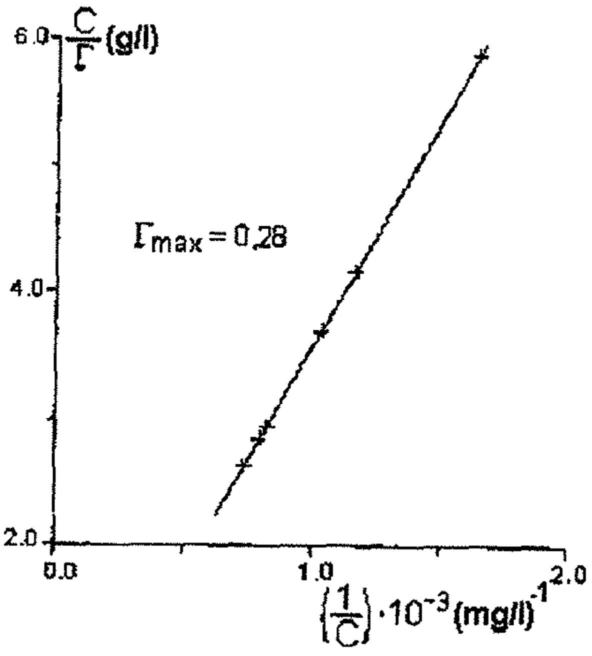


Fig. 5. Langmuir plot of manganese sorption onto *P. aeruginosa*

Tab. 2. Chemical composition of *P. aeruginosa* call-wall (11)

Amino-acids (g/100 g wall)	Monosaccharides present	Major classes of cell-wall constituients	Chemical composition
Alanine 5.1			
Arginine 1.3	Glucose	Proteins	
Aspartic acid 9.3	Fucose	Polysaccharides	%N %P %S_{red}
Phenylalanine 7.3	Rafinose	Lipids	1.4-10.1 1.6-1.7 8.0-12.1
Glycine 7.1			

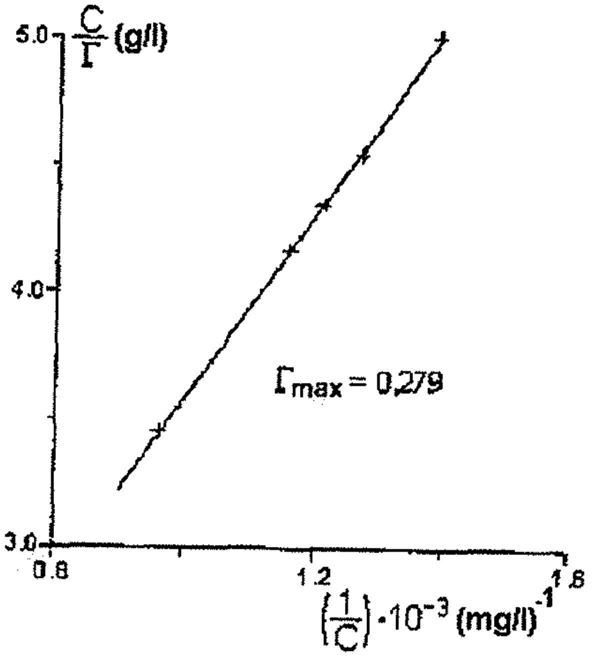


Fig. 6. Langmuir plot of manganese sorption onto *S. cerevisiae*

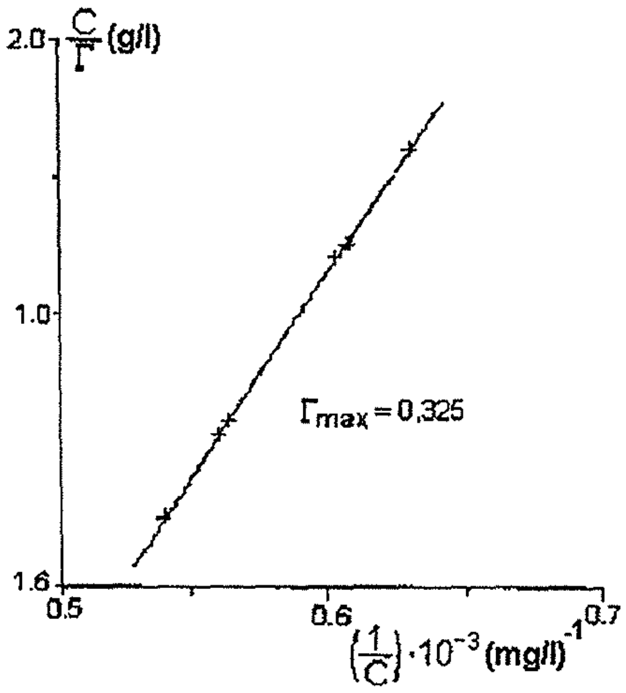


Fig. 7. Langmuir plot of zinc sorption onto *B. subtilis*

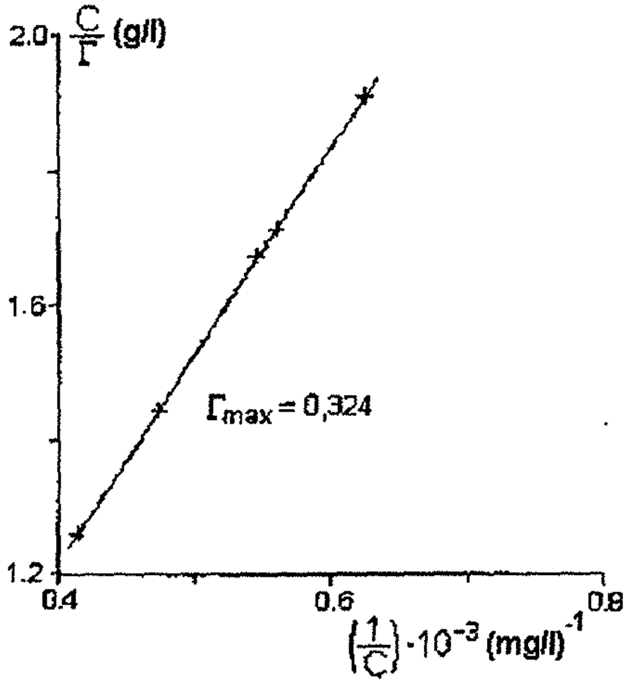


Fig. 8. Langmuir plot of zinc sorption onto *P. aeruginosa*

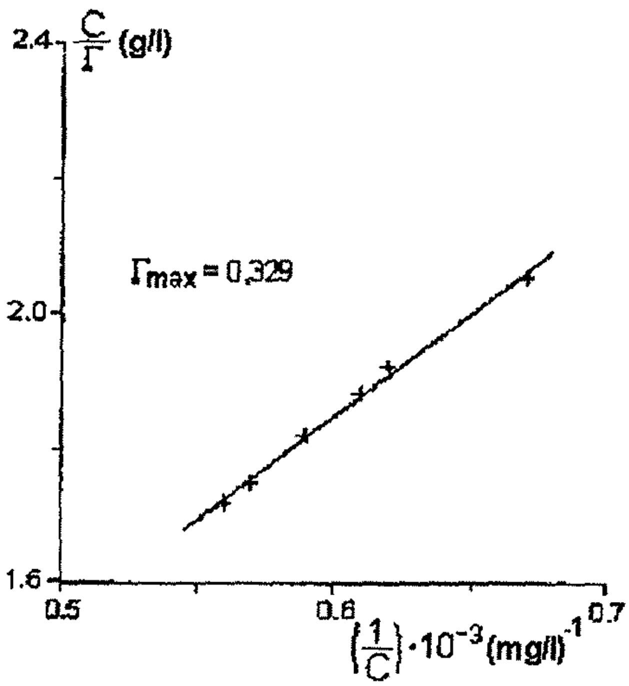


Fig. 9. Langmuir plot of zinc sorption onto *S. cerevisiae*

Most microorganisms are adopting different strategies for decreasing metal ion toxicity, strategies which are almost completely unknown at molecular levels. The metal toxicity can be decreased either through extracellular deposition as a insoluble form (like sulphide, oxalates, citrates etc.) or by through the intracellular deposition in the presence of varied proteins.

CONCLUSIONS

The positive adsorption of these three cations (Fe, Mn, Zn) by the microbian species (*B. subtilis, P. aeruginosa, S. cerevisiae*) followed the Langmuir isotherm, indicating a single layer adsorption to the cell-wall surface [6]. The process is develop by cations substitution from the initial solutions and their concentration to the cell-wall surface (bioadsorption) or inside the cell (bioaccumulation) [7], until the chemical equilibrium between adsorption and desorption is attained.

The adsorption isotherm may characterize the accumulation processes of metallic cations from solutions. Thus, *B. subtilis* and *P. aeruginosa* seems to be nonspecific for the adsorption of Fe and Mn cations. For Zn adsorption the values of Γ_{max} are bigger as a result of the detoxification process at high concentrations. A transmembrane-transport process with precipitation as a metal-protein may occur for Zn.

At high concentration of metallic ions the adsorptions process for *P. aeruginosa* presents a sigmoidal type curve, which show that the kinetics process is more complex and the graphical representation followed a different Langmuir curve [6].

Although the adsorption process by *S. cerevisiae* occurs with good yields for the subjected cations, the results obtained by the authors, did not confirm those from literature (they present lower values). The literature present *S. cerevisiae* as a good and rapid adsorbant of metallic cations, even at high concentrations.

The results obtained allow us to conclude that the method may be applied to real systems, which involve the adsorption of metallic cations from mine waters, waste waters etc. The originality of the work lies in the comparative biosorption study of the microorganisms considered for analysis.

ACKNOWLEDGEMENTS

The authors are grateful to Miss S. Dunca, Department of Microbiology, University "Al. I. Cuza" Iasi, for her technical assistance.

REFERENCES

1. A. E. Torma and K. Bosecker, *Prog. Ind. Microbiol.*, **16**, 77-118, (1982).
2. A. G. Lundgren and M. Silver, *Ann. Rev. Microbiol.*, **34**, 263-283, (1980).
3. R. Mocanu, I. Miu, T. Gavriloaiei, *Euroanalysis IX, Eur. Conf. on Anal. Chemistry*, Bologna, 1-7 sept, FECS, P45, (1996).
4. O. Ailisei, E. Nimiţan, St. Comănescu, *Lucrări practice de microbiologie generală*, Universitatea "Al.I.Cuza" Iaşi, (1980).
5. V. Isac, A. Onu, C. Tudoreanu, Gh. Nemtoi, *Chimie fizica, lucrari practice*, Ed. Stiinta, Chisinau, (1995), pp. 575-605.
6. G. M. Gadd and L. de Rome, *Apll. Microbiol. and Biotechnol.*, **29**, 610-617, (1988).
7. G. W. Strandberg, S.E. Shumate II, J.R. Parrett, Jr., *Appl. Environ. Microbiol.*, **41**,237-245, (1981).
8. T. G. Beveridge and R.G.E. Murray, *J. Bacteriol.*, **127**, 1502-18, (1976).
9. T. G. Beveridge and R.G.E. Murray, *J. Bacteriol.*, **141**, 876-87, (1980).
10. M. N. Hughes and R. K. Poole, *Metals and Microorganisms*, Chapman and Hall, London, New York, (1989), pp. 257-358.
11. M. R. J. Salton, *The Bacterial Cell Wall*, Elsevier Publishing Co., Amsterdam, London, New York, (1964).
12. N. Kuyucak and B. Volesky, *Biorecovery*, **1**, 189-204, (1988).

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, N° 6, 1998

EXTRACTION OF COLORED SUBSTANCES FROM MATÉ (ILEX PARAGUARIENSIS)

Vania Regina Gabbi Polli[a], Alnei Ramos Prochnow[a] and Juliane Zimmerman Tamanini[b]
Departamento de Física (Físico-Química)[a]
Centro de Ciências Naturais e Exatas
Curso de Engenharia Química[b]
Centro de Tecnologia
Universidade Federal de Santa Maria
Santa Maria, RS, Brazil

ABSTRACT

Liquid-liquid extraction of pigments present in maté (Ilex Paraguariensis) was studied using various organic solvents and different connterions. The best results were obtained using diethyl ether and sodium lauryl sulfate. The effect of the addition of ethanol on the extraction process was also analyzed.

KEY WORDS: Maté (Ilex Paraguariensis), liquid-liquid extraction, saponins, sodium lauryl sulfate, pigments.

RESUMO

Foram estudados sistemas de extração liquido-liquido para os corantes da erva mate, testando-se vários solventes orgânicos e diferentes contra-íons. O melhor sistema extrator foi éter dietilico-lauril sulfato de sódio. O efeito da adição de etanol sobre o sistema também foi estudado.

INTRODUCTION

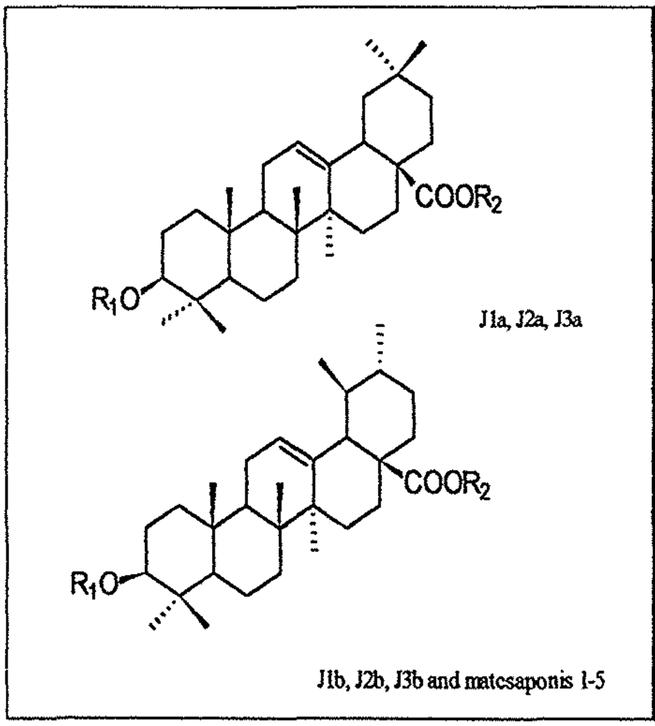
The maté beverage ("mate" or "chimarrão") is widely used in Southern Brazil, Argentina, Paraguay and Uruguay and it is an integral part of the "Gaúcho" culture. It is also widely used as a medicinal plant, having stimulant, diuretic, antirheumatic and antinflammatory properties. The genuine maté comes from Ilex Paraguariensis Saint Hilaire, a South American native perennial tree coming from the holly family.[11] According to Gaucho tradition, the ceremony of drinking maté (tea), passing the "cuia" (a receptacle made from a native pumpkin) among the participants leads to an atmosphere of respect, friendship and solidarity and at the same time the tea is efficient against food intoxications and acts as a general tonic.[1-3]

The main active components of maté (erva mate) are saponins, more specifically they are glycosides of ursolic and oleanolic acids.[3-5] Their general structure is given in Figure 1. The isolation procedure usually involves the extraction of dried and ground leaves by maceration in CH_3CH_2OH-H_2O followed by successive extraction with CH_2Cl_2 and n-butanol and repeated column chromatography. The structure determination is usually done using ^1H and ^{13}C nuclear magnetic resonance, mass spectra and visible and ultraviolet spectroscopy, known secondary

DOI: 10.48141/SBJCHEM.v6.n6.1998.47_1998.pdf

metabolites are xanthines (mainly caffeine), flavonoid glycosides (rutin) and caffeoylquinic acid derivatives or chlorogenic acids.[3]

The purpose of the present work was to study some rapid methods for the extraction of pigmented or colored substances present in maté beverage (tea). It is well Known that compounds with formal positive or negative charge can be readily extracted with organic solvents through ion-pair formation using connterions. This method has been widely used for the extraction of artificial dyes in industrialized foods and in phase transfer catalysis.[7,8] Surfactants have often been used as phase transfer agents.[6-9]



J1a R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=H
J1b R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=H
J2a R1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl; R_2=H
J2b R1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl; R_2=H
J3a R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=β-D-glucopyranosyl
J3b R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=β-D-glucopyranosyl

Matesaponin 1 R_1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl
R_2=β-D-glucopyranosyl

Matesaponin 2 R_1=β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl;
R_2=β-D-glucopyranosyl

Matesaponin 3 R1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl;
R_2=β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl

Matesaponin 4 R1=β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl;
R_2=β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl

Matesaponin 5 R1=β-D-glucopyranosyl-(1→3)-[α-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl;
R_2=β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl

Structures of the saponins isolated from Ilex paraguariensis.(3)

FIGURE. 1. General Strutura of the Saponiuns Isolated from Ilex paraguariensis.

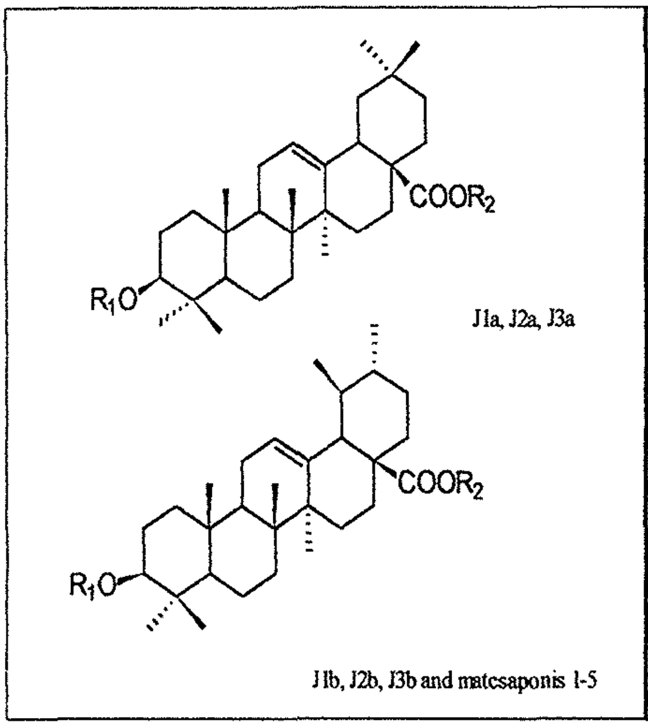
Liquid-liquid extraction is on experimental technique where a solution (usually aqueous) is placed in contact with a second solvent (usually an organic solvent), essentially immiscible in the first one, with the purpose to transfer one or move solutes from the first solvent to the second one. The separations are usually simple, clean, rapid and practical. In many cases the separation may be done by simple agitation during a few minutes using a separatory funnel.

One would not expect that it would be possible to extract organic compounds from aqueous solutions with organic solvents, because there would be a large loss of energy of electrostatic solvation. The most obvious way to make an aqueous ionic species extractable is to neutralize its charge. This can be attained by the formation of a neutral metal chelate complex or by ionic association, i.e., ion-pairing. The more hydrophobic the resulting molecule, the better its extraction.[10,12] An alternative is the solubilization of the pigments with micelles.

In spite of the fact the consumption of maté is significant in the southern part of Latin America, systematic research in this subject is still in an incipient stage and our effort represents a step is this direction.

metabolites are xanthines (mainly caffeine), flavonoid glycosides (rutin) and caffeoylquinic acid derivatives or chlorogenic acids.[3]

The purpose of the present work was to study some rapid methods for the extraction of pigmented or colored substances present in maté beverage (tea). It is well Known that compounds with formal positive or negative charge can be readily extracted with organic solvents through ion-pair formation using connterions. This method has been widely used for the extraction of artificial dyes in industrialized foods and in phase transfer catalysis.[7,8] Surfactants have often been used as phase transfer agents.[6-9]



J1a R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=H
J1b R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=H
J2a R1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl; R_2=H
J2b R1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl; R_2=H
J3a R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=β-D-glucopyranosyl
J3b R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=β-D-glucopyranosyl

Matesaponin 1 R_1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl
R_2=β-D-glucopyranosyl

Matesaponin 2 R_1=β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl;
R_2=β-D-glucopyranosyl

Matesaponin 3 R1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl;
R_2=β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl

Matesaponin 4 R1=β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl;
R_2=β-D-gluoopyranosyl-(1→6)-β-D-glucopyranosyl

Matesaponin 6 R1=β-D-glucopyranosyl-(1→3)-[α-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl;
R_2=β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl

Structures of the saponins isolated from **Ilex paraguariensis**.(3)

FIGURE. 1. General Strutura of the Saponiuns Isolated from Ilex paraguariensis.

Liquid-liquid extraction is on experimental technique where a solution (usually aqueous) is placed in contact with a second solvent (usually an organic solvent), essentially immiscible in the first one, with the purpose to transfer one or move solutes from the first solvent to the second one. The separations are usually simple, clean, rapid and practical. In many cases the separation may be done by simple agitation during a few minutes using a separatory funnel.

One would not expect that it would be possible to extract organic compounds from aqueous solutions with organic solvents, because there would be a large loss of energy of electrostatic solvation. The most obvious way to make an aqueous ionic species extractable is to neutralize its charge. This can be attained by the formation of a neutral metal chelate complex or by ionic association, i.e., ion-pairing. The more hydrophobic the resulting molecule, the better its extraction.[10,12] An alternative is the solubilization of the pigments with micelles.

In spite of the fact the consumption of maté is significant in the southern part of Latin America, systematic research in this subject is still in an incipient stage and our effort represents a step is this direction.

EXPERIMENTAL PROCEDURE

Liquid-liquid extraction was performed an “cold tea of erva mate”(aqueous solutions at room temperatura) in the presence or absence of ethanol using various organic solvents such as diethyl ether, methanol, n-propanol, n-butanol, chloroform, etc and counter-ions of NaLS (sodium lauryl sulfate), CPCl (cetylpyridinium chloride) and CTAB (cetyltrimethylammonium bromide) at concentrations ranging from 0,4 x 10^{-3} M to 6,0 x 10^{-3} M.

All the reagents used were of analytical reagent grade and the water was deionized and distilled. The erva mate employed was always of the same commercial brand (Raizes).

The absorption spectrum of the extracts was determined in the visible region (500-700 nm) using a Carl Zeiss spectrophotometer.

RESULTS AND DISCUSSION

Typical absorption spectra obtained for the extract using the three different surfactants or phase transfer agents are shown in Figure 2. As can be seen, NaLS, na anionic species, is by far the most efficient as far as extraction is concerned. The maximum absorption band is present at 680 nm and was subsequently used as a criterion for the best extraction.

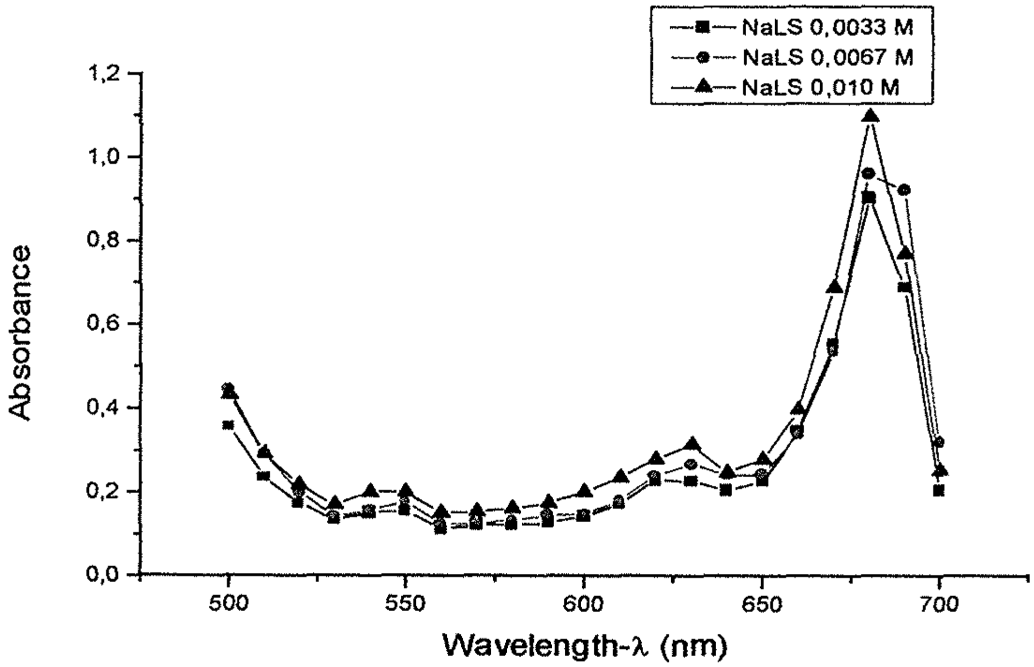


FIGURE 2. Absorption Spectrum of the Pigments of Erva Mate Using Diethyl Ether and Various Phase Transfer Agents.

Figure 3 illustrates the absorption spectra obtained for the extracts using NaLS (0,003 M) and diethyl ether and butanol as organic solvents.

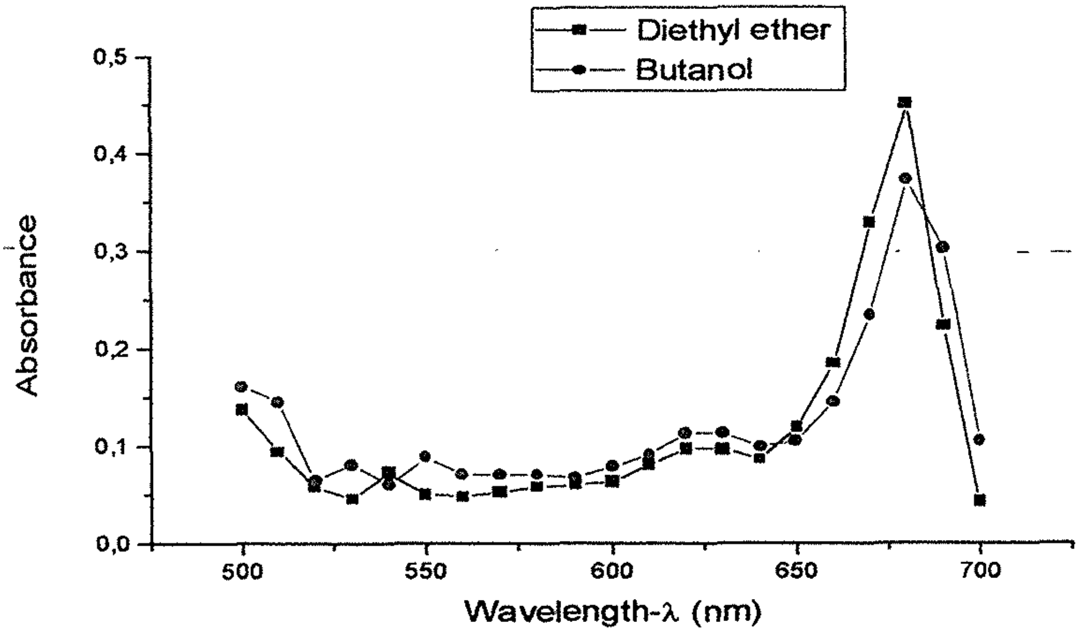


FIGURE 3. Absorption Spectrum of the Pigments of Erva Mate Using NaLS (0,003 M) and Diethyl Ether or Butanol as Organic Solvents.

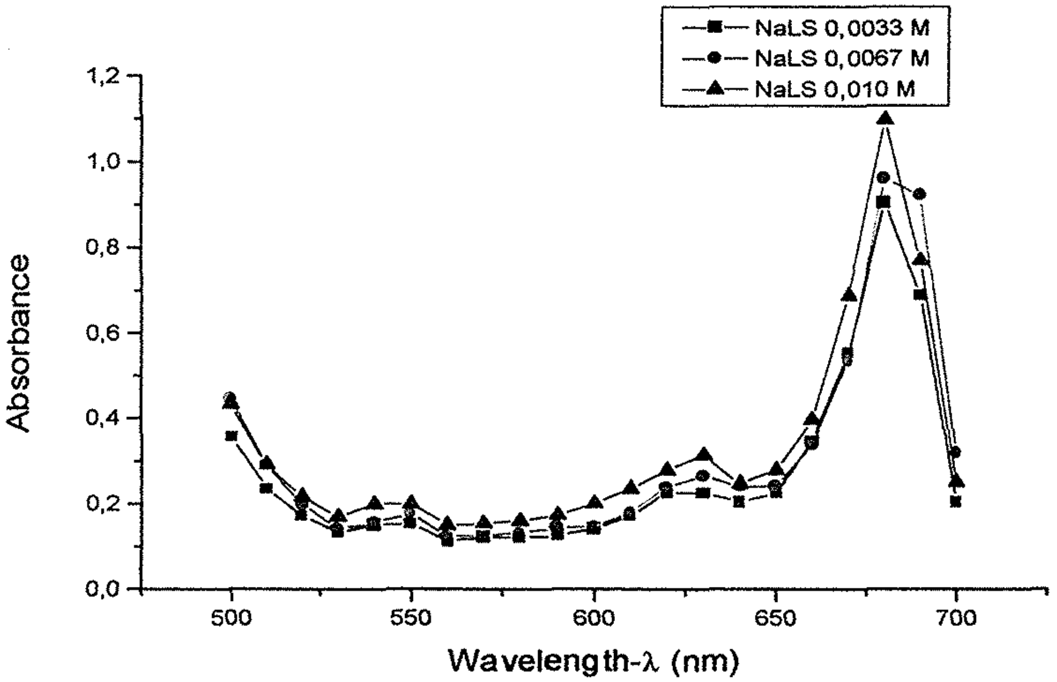


FIGURE 4. Absorption Spectrum of the Pigments of Erva Mate Extracted with Diethyl Ether and Different Concentrations of Sodium Lauryl Sulfate (NaLS).

The effect of the concentration of sodium lauryl sulfate (NaLS) on the extraction process is shown in Figure 4. In all cases shown in the figure, the surfactant is present in concentrations above the CMC (critical micellar concentrations). However we also observed extraction when the surfactant was below the CMC, indication the ion-pair formation and subsequent phase transfer is also important.

The effect of the addition of ethanol on the extraction of pigments with diethyl ether and sodium lauryl sulfate (NaLS) is illustrated in Figures 5 and 6.

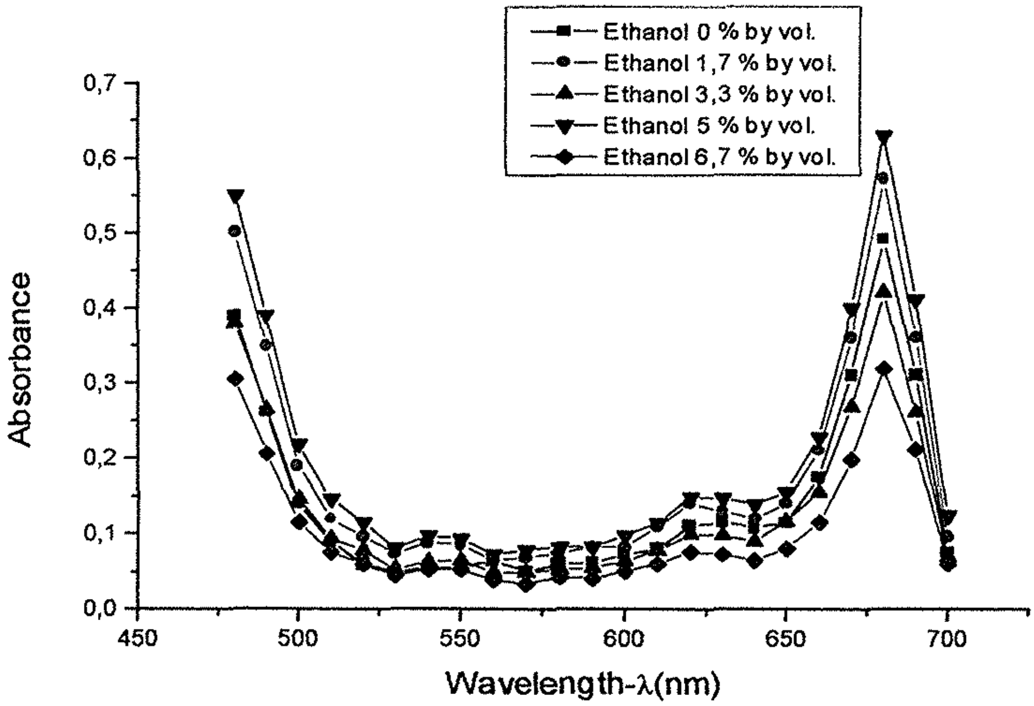


FIGURE 5. Absorption Spectrum of Pigments Extracted from Erva Mate Using Diethyl Ether, Sodium Lauryl Sulfate (NaLS) and of Low Concentrations of Ethanol.

The experimental results clearly show that the addition of ethanol at low concentrations (around 5 to 6 percenthy volume) improves the extraction process. At higher concentrations however, (more than 10%) the extraction process is hindered. The effect of ethanol may be explained by its effect on micelle formation.

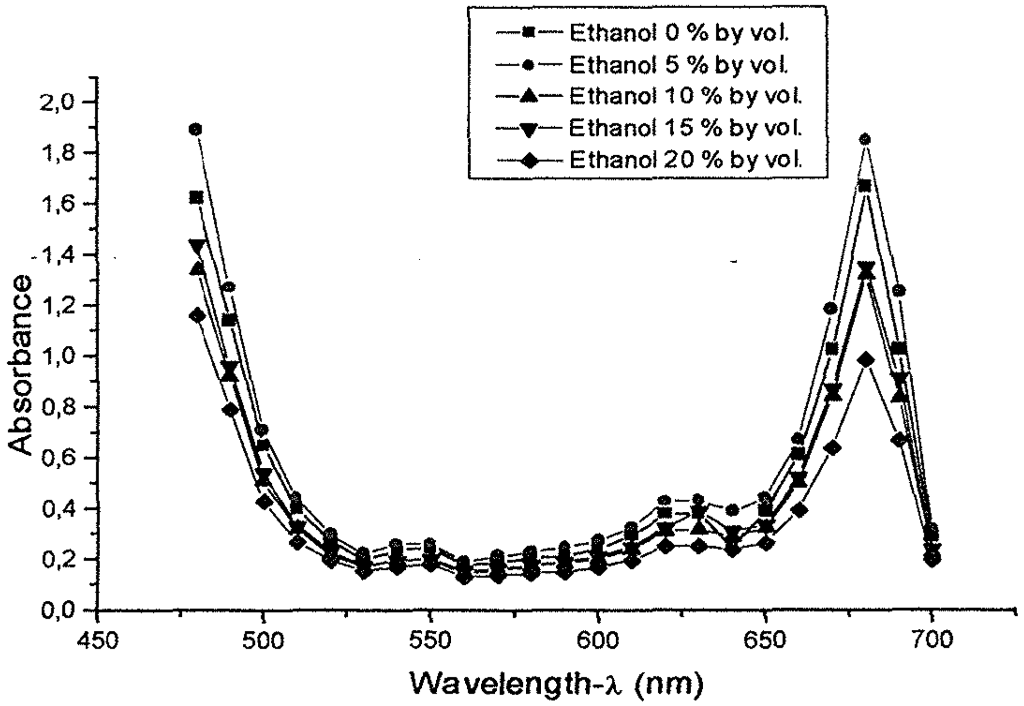


FIGURE 6. Absorption Spectrum of Pigments Extracted from Erva Mate Using Diethyl Ether, Sodium Lauryl Sulfate (NaLS) and a Wide Range of Concentrations of Ethanol.

CONCLUSION

It may be concluded that the pigments of erva mate may be extracted easily from aqueous solutions by using sodium lauryl sulfate, diethyl ether and low concentrations of ethanol. Further studies are in progress to elucidate the structure of these colored substances.

REFERENCES

1. F.E. Staff, "Erva Mate", Curso de Engenharia Florestal, Universidade Federal de Santa Maria, Santa Maria, RS, 1982.
2. K.H. Kraemer, A.T.C. Taketa, E.P. Schenkel, G. Grosmann and D. Guillaume, Phytochemistry, 42(4), 1119 (1996).
3. E.P. Shenkel, G. Gosmann, J.A. Montanha, B.M. Heizmann, M.L. Athayde, A.T.C. Taketa, V.S. Pires and D. Guillaume, Ciência e Cultura Journal of the Brazilian Association for the Advancement of Science, 49(5/6), 359 (1997).
4. B.M. Heinzmann and E.P. Shenkel, J. Nat. Prod., 58, 1449 (1995).
5. R. Filip and D.I.A. De Iglesias, Acta Farm. Bonaerense, 2, 87 (1983).
6. P.S. Bonato, R.S. Silva, T. Shuhama, L.F.L. Guimarães and J.R. Jabor, Química Nova, 16(3), 177 (1993).
7. R.A. Jones, Aldrichimica Acta, 9, 35 (1996).
8. M. Ma Kosza, Tetrahedwn Lett., 5489 (1966).
9. L.G. Ionescu and B.J. Czerniawski, Rev. Roum. Biochim., 18, 103 (1981).
10. V.R.M Gabbi Polli, Master's Thesis, Universidade Federal de Santa Catarina, Florianópolis, S.C., Brazil, 1981, 75 pp.
11. H. Winge, A.G. Ferreira, J.E.A. Mariath and L.C. Tarasconi, "Erva-Mate, Biologia e Cultura no Cone Sul", Editora da Universidade, UFRGS, Porto Alegre, RS, Brasil, 1995.
12. J. Basset, R.C. Denney, G.H. Jeffrey, J Mendham and J. Vogel, "Análise Inorgânica Quantitativa", Guanabara Dois, Rio de Janeiro, RJ, Brazil, 1981.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, N° 6, 1998

New Complexes of Pr(III),Sm(III),Gd(III),Ho(III),La(III) 1-(2'-Benzthyazolyl)-3-methyl-4-azo-(4''-nitrophenyl)-Pyrazolyn-5-one

Anca Emandi*,Mariana Balasoiu,Tudor Rosu***
*Faculty of Chemistry,Bucharest University,Dumbrava Rosie 23,sector 2, 70609 Bucharest,Romania
**Institute of Physical Chemistry of Romanian Academy,Splaiul Independentei 202, 77208 Bucharest, Romania.

ABSTRACT

1-(2'-Benzthyazolyl)-3-methyl-4-azo-(4''-nitrophenyl)-Pyrazolyn-5-one (HL) possesses a chelating behaviour.Its chelates with a number of trivalent lanthanide ions Pr(III), Sm(III),Gd(III), Ho(III),La(III) of the type $Na_3[Ln(L)_2(OH)_4]$ have been isolated and characterized on the basis of their elemental analyses,IR and visible spectra,magnetic and molar conductance studies,thermal and X-ray analysis and molecular weight determinations.All chelates have a monomeric octa-coordinated structure and square antiprismatic (C_2) symmetry.

KEYWORDS **Lanthanides complexes; Azodye; Pyrazolyn-5-one; UV-VIS; IR spectroscopy.**

RESUMO

1-(2'-Benztiazolil)-3-metil-4-azo-(4"-nitrofenil)-pirazolin-5-ona (HL) é um bom ligante. Forma complexos do tipo $Na_3/LnL_2(OH)_4/$ com íons trivalentes de lantanídeos como Pr(III), Sm(III), Ho(III) e La(III). Estes complexos foram isolados e caracterizados usando análise elementar, determinação de peso molecular, espectroscópia no visível e infravermelho, condutância magnética e molar, raios-x e análise térmica. Todos os quelatos tem estrutura octa-coordenada e possuem simetria quadrado antiprismática (C_2).

DOI: 10.48141/SBJCHEM.v6.n6.1998.55_1998.pdf

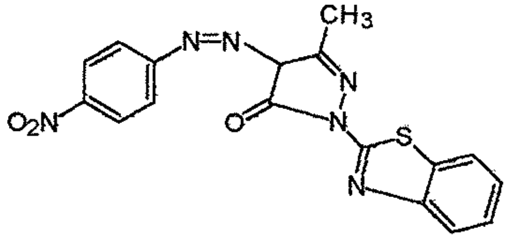
Introduction

A perusal of literature[1-4] reveals numerous ligands containing azo group -N=N-,the nitrogen of which coordinates to the metal ions.The arylazopyrazolones are commonly used in food coloring and in the production of magenta dyes in various color photographic processing[5-6].The effect of various types of Lewis bases in combination with 4(p)-nitrobenzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-5-one (NMPP) on the extraction of Eu(III) and Nd(III) has also been studied[7].

A method has been developed for the rapid determination of small amounts of Nd.,Ho,Er,Tm in a mixture of lanthanides with arylazopyrazolones derivatives[8-9].

The survey of the literature data revealed that hardly any data is available on the stereochemical properties of these complexes but a study of their spectral and magnetic behaviour[10-11]can poit out some of these properties.

In the present investigation,a number of five trivalent lanthanide ion complexes of 1-(2'-Benzthyazolil)-3-methyl-4-azo-(4'-nitrophenyl)-Pyrazolin-5-one structure (I) were prepared and characterized by a variety of spectral and analytical methods to clarify the structure as well as the nature of the bonding in these complexes in the solid state.



Structure (I)

This ligand is a good pigment for rubber,and we expect semiconductor properties for these complexes.

Experimental

Apparatus and Reagents

Elementary analyses were obtained with a CARLO ERBA EA 1108.Ln^{3+} concentrations were determined by gravimetric methods.

Magnetic moments were determined by Gouy's technique and diamagnetic corrections were calculated from Pascal's constans.

Conductivity measurements were carried out using a Wescan 212 conductivitity meter in N,N-dimethylformamide (DMF) 10^{-3}M at room temperature.

Molecular weights were determined in chloroform at 37°C with a Mechlorab Model 301A vapor pressure osmometer.The concentration of the solution were in the range of 10^{-3}-10^{-4}M.

The electronic spectra of all compounds were obtained by the diffuse-reflectance technique,dispersing the sample in MgO ,with a Specord M 400 Carl Zeiss Jena Spectrophotometer.

The IR spectra were run with a Perkin Elmer FT-IR spectrophotometer in the range of 4000-200 cm^{-1} in KBr pellets and in the range of 12000- 4000 cm^{-1} in solid state with a Cary 17D (NIR).

The gadolinium complex was studied by thermogravimetric(TG) and differential thermal analysis (DTA) in a static air atmosphere, with sample heating of 5^0/min using a MOM-Budapest OD 103 Paulik Evdey derivatograph.

The final residue was studied with X-rays using a HZG Diphractometer, with CoK_α radiations and Cu, Fe filter and TUR-M 62 generator, v=0.5^0/min,$6*10^4$imp/min.

All compounds and solvents were pure BDH grade chemicals.The ligand used was prepared according to a method described in the literature [12].

Preparation of lanyhanide complexes

Aqueous solution of lanthanide (III) chlorides (1.5×10^{-3}mole and 5 ml H_2O) were mixed with ethanolic suspensions of the ligand (3×10^{-3}mole in 10 ml ethanol) in a ratio M:L=1:2.After half an hour the pH of the reaction mixture was adjusted from 4.5 to 8 with aqueous $CH_3COONa.3H_2O$(3×10^{-3}mole) and the reaction mixture was refluxed for an hour.After an hour of reflux the pH of the reaction mixture was adjusted to 9 - 9.5 with aqueous solution 4% NaOH and was refluxed for half an hour.The product obtained on cooling was filtered off, washed succesivelly with ether and finnaly was recrystallized from an mixture of water : ethanol,1:2(v/v).

Results and Discussion

Elementary analysis shows a ratio lanthanide :ligand of 1:2.The molar conduntance values (200-240 Ω^{-1} cm^2 mol^{-1}) in DMF 10^{-3} M shows a 1/3 electrolyte behavior of the complexes.The analytical results shows a geneal formula $Na_3[Ln(C_{17}H_{11}N_6O_3S)_2(OH)_4]$ for the complexes .,where Ln=Pr(III),Sm(III),Gd(III),Ho(III)and La(III) (Table 1).

The thermal decomposition(Figure 1) is in good agremeent with literature data [14,15] and shows no coordinated water molecules,because in the range 120-190^{0}C there isn't a Loos through an endothermicprocess.In the third stage there are two exothermic effects 495^{0}C And 510^{0}C which represent NaOH elimination.In the third stage there are two exothermic effect at 560^{0}C corresponds to Gd_2O_3 formation.

The X-ray spectrum (Figure 2)is in good agreement with the presence of Gd_2O_3.

Magnetic moments .Allcoordination compounds under study except the La(III)-complex are paramagnetic while the latter is diamagnetic because of the presence of unpaired electrons in the 4f subshells,wich are shielded by 5s,5p and 5d orbitals .This makes it very difficult for the ligands to attack the inner 4f electron . Therefore ,the magnetic moments of the complexes should be affected to a lesser extent as compared to that of the metal salt itself.There is a slight variation in the experimental magnetic moment values (Table 1) which may be due to the thermal population of excited states whose degenerate levels have been split by the crystal field[16].

The molecular weight determinations show the complexes to be monomers .

The IR spectra of the bidentate azodye ligand and its complexes are quite informative .The IR spectra of the ligadd[16](Table 2) shows a band at 1642 cm^{-1} due to ν(C=O) group of the pyrazolone ring and a strong band at 1526 cm^{-1} due to [ν(N=N)+ν(C=N)] and a band at 1433 cm^{-1} assigned as ν_{as}(N=N).The positions of these bands are highly influenced by the nature of the substituent in the aryl ring.Their shifts to longer wavelengths are due to increasing overlap of the molecular orbitals of the N=N system.The strong band at 1343 cm^{-1}

Table 1. Analytical, molar conductance, magnetic moments data of the trivalent lanthanide ions complexes

Complex	Microanalysis Results				λ $\Omega^{-1}cm^2mol^{-1}$	μ_{eff} [BM]	Mol wt	Powder colour
	C %	H %	N %	Ln %				
$Na_3[La\,(C_{17}H_{11}N_6O_3S)_2\,(OH)_4]$	(39.46)* 40.01	(2.12) 3.00	(16.24) 16.25	(13.43) 13.50	240.01	(-) 0.25	1033.91	orange
$Na_3[Ho\,(C_{17}H_{11}N_6O_3S)_2\,(OH)_4]$	(33.30) 33.75	(1.79) 2.00	(13.71) 13.82	(13.46) 13.63	220.42	(4.89) 4.60	1224.86	brown -orange
$Na_3[Gd\,(C_{17}H_{11}N_6O_3S)_2\,(OH)_4]$	(38.77) 39.05	(2.09) 2.85	(15.96) 16.01	(14.94) 15.02	235.40	(7.94) 7.86	1052.25	brown -orange
$Na_3[Sm\,(C_{17}H_{11}N_6O_3S)_2\,(OH)_4]$	(39.02) 40.01	(2.10) 2.55	(16.07) 16.00	(14.38) 14.65	236.80	(5.91) 5.82	1045.35	brown -orange
$Na_3[Pr\,(C_{17}H_{11}N_6O_3S)_2\,(OH)_4]$	(39.38) 40.11	(2.12) 2.70	(16.21) 16.45	(13.60) 13.82	238.75	(2.83) 2.78	1035.91	brown -orange

* (Calculated) Experimental

Table 2. The IR (cm^{-1}) spectral data of the HL ligand and the $Na_3[Ln(L)_2(OH)_4]$ complexes (Ln = La^{III}, Pr^{III}, Sm^{III}, Gd^{III}, Ho^{III})

Assignements	Compounds					
	HL	$Na_3[La(L)_2(OH)_4]$	$Na_3[Pr(L)_2(OH)_4]$	$Na_3[Sm(L)_2(OH)_4]$	$Na_3[Gd(L)_2(OH)_4]$	$Na_3[Ho(L)_2(OH)_4]$
ν(C=O) of pyrazolon ring	1642	-	-	-	-	-
ν(C=N)+ ν(C=O) ν_{as}(C=O)	1526 1433	1467	1468	1468	1470	1470
ν(OH) in hydroxo complexes	-	3445	3442	3444	3444	3445
δ(M-O-H)	-	1183	1183	1183	1183	1183
ν(C=O) enolic coordinated	-	1320	1322	1322	1324	1324
O-H...N	3457	-	-	-	-	-
ν(M-O)	-	470	472	475	475	475
ν(M-N)	-	529	530	530	530	530

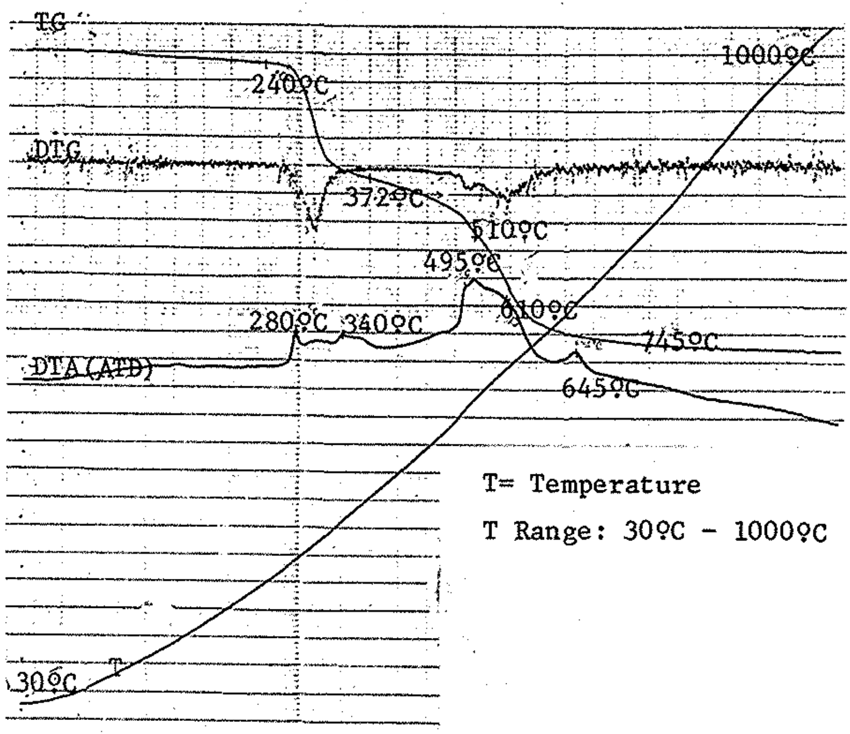


Figure 1.The differential thermogravimetric (DTG), thermogravimetric (TG) and differential thermal (ATD)analysis of the $K[Gd(L_2)(H_2O)_2]$ complex.

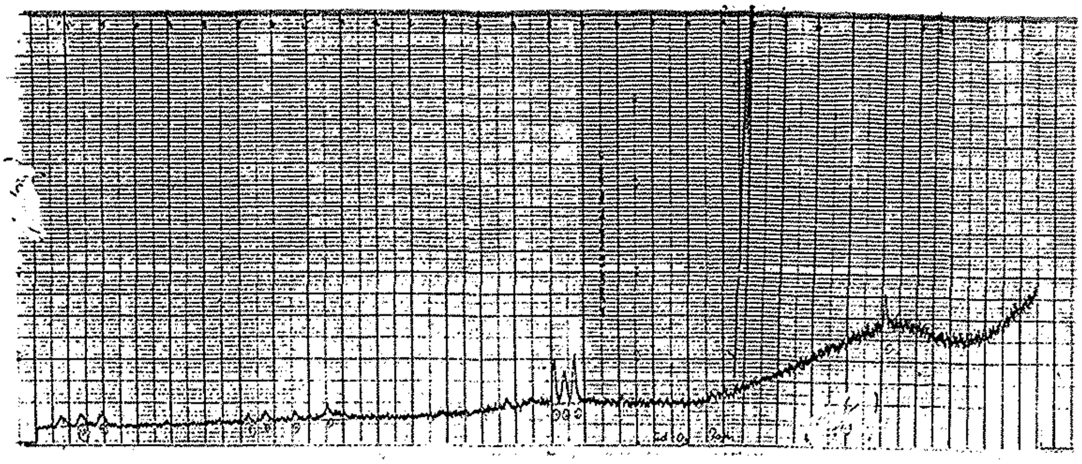
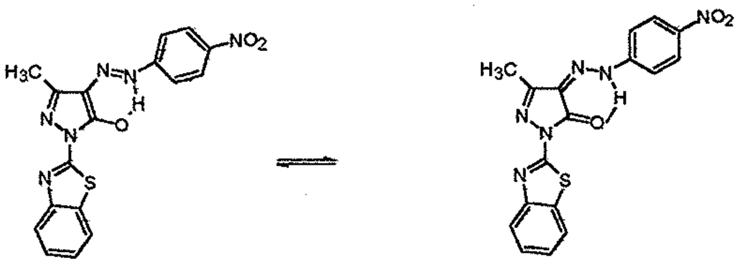


Figure 2.The X-ray spectrum of the $K[Gd(L_2)(H_2O)_2]$ complex.

can be attributed to the stretching ν of the (C-OH) group .The broad strong band at 3457 cm^{-1} is explained by the presence of an associate NH and OH hydrogen bond . It is clear from these data that the ligand certanly exists as azoenol –hydrazoketo tautomeric structures:



Azoenol form   Hidrazoketo form

The IR spectra (Table 2) of the complexes exhibit a band at 3445cm^{-1} assignable to the OH stretching and a band at 1183 cm^{-1}assignable to the M-O-H bending in hydroxocomplexes of lanthanide ions and these data are in good agreement with the literature values[17].

The weak band at 1320cm^{-1}may be assigned to the enolic ν(C-O) coordinated to the metal ions[18].In all the metal complexes there are no bands corresponding to coordinated water molecules.In the metal chelates the band at 3457cm^{-1} due to intramolecular O-H……N[18] disappears showing the deprotonation of enolic hydroxyl group.The sharp band at 1526cm^{-1} in the azo dye due to [ν(N=N) and ν(C=N)] shifts to 1467cm^{-1} upon complexation indicating the bonding of one of the azo nitrogen atoms to the metal atoms[19,20].

The conclusive evidence of bonding is confirmed by the occurrence[21] of ν(M-O) and ν(M-N) bands at about 470cm^{-1} and 529cm^{-1},respectively.

Hence the azo dye behaves as monovalent and bidentate ligand bonded through the potential donor (N –O) atoms in azoenolic form.

In the UV-VIS region of the ligand the following bands appear : (nm) 387(-N=N-),225(C=N),270(aromathic ring) and 280(C=O) of the pyrazolone ring[12].In the complexes these bands are shifted as following :(nm) 365(-N=N-),325(C=N),265(aromathic ring) and the at 280 nm disappears because the π-bonding of (C=O) of the pyrazolone ring is quenched[19].

The electronic spectra of the lanthanide complexes are the same as in aqueous solution of the lanthanides cation Ln^{3+} because the **f-f** transition are not influenced by the neighbours[22].In our lanthanides complexes all the bands are shifted compared with Ln^{3+}(aqueous).The bands between 16000-20000cm^{-1} are very sensitive to the coordination number.Inthis region we discovered bands in good agreement with the octacoordinated Ln^{3+}.

$[PrL_2(H_2O)_2]$. We found the following transitions:

16900 cm^{-1} for $^3H_4 \rightarrow {}^1D_2$ (in Pr^{3+}(aq) 16980 cm^{-1})

20200 cm^{-1} for $^3H_4 \rightarrow {}^3P_0$ (in Pr^{3+}(aq) 20700 cm^{-1})

. 20850 cm^{-1} for $^3H_4 \rightarrow {}^1I_6$ (in Pr^{3+}(aq) 21500 cm^{-1}).This transition is sensitive to the number of neighbours and it is in a good agreement with the octa-coordination of Pr^{3+}.The band at the 33300cm^{-1} corresponds to the transition $4f^n \rightarrow 4f^{n-1}d$ [23,24](Figure 3).

$[SmL_2(H_2O)_2]$. We found the following bands :

17450 cm^{-1} for $^6H_{7/2} \rightarrow {}^4G_{5/2}$ (in Sm^{3+}(aq) 17880 cm^{-1})

18340 cm^{-1} for $^6H_{7/2} \rightarrow {}^4F_{3/2}$ (in Sm^{3+}(aq) 18880cm^{-1})

. 20400 cm^{-1} for $^6H_{7/2} \rightarrow {}^4G_{7/2}$ (inSm^{3+}(aq) 19950cm^{-1}) (Figure 4).

The hyper sensitive transition to $^6F_{1/2}$ appears in NIR range at:

5995 cm^{-1} for $^6H_{7/2} \rightarrow {}^6F_{1/2}$ (in Sm^{3+}(aq) 6200cm^{-1})

6305 cm^{-1} for $^6H_{7/2} \rightarrow {}^6H_{15/2}$ (in Sm^{3+}(aq) 6460cm^{-1})

. 6468cm^{-1} shoulder for $^6H_{7/2} \rightarrow {}^6F_{3/2}$ (inSm^{3+}(aq) 6640cm^{-1})

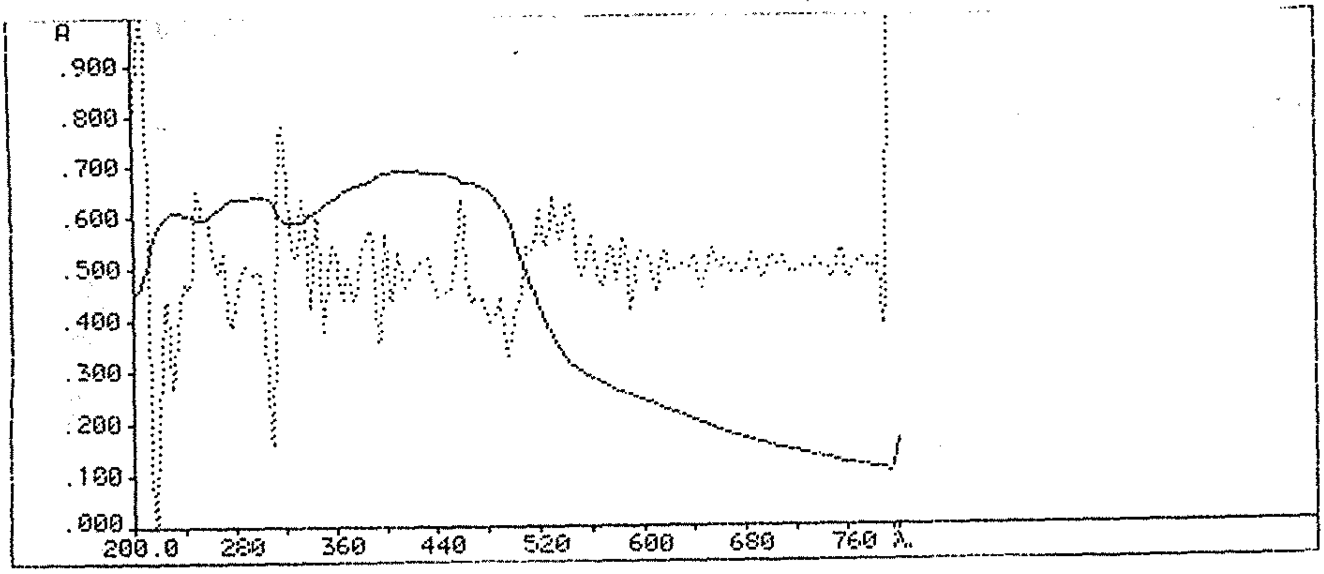


Figure 3. The UV-VIS (nm) spectrum of the K[Pr(L_2) (H_2O)$_2$] complex

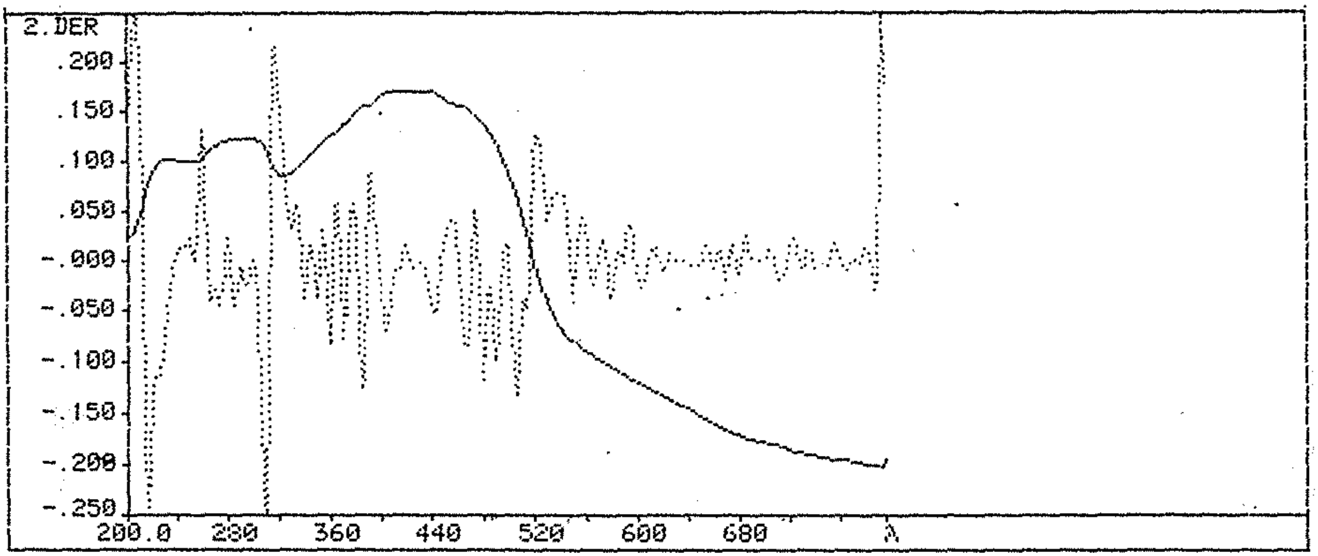


Figure 4. The UV-VIS (nm) spectrum of the K[Sm(L_2) (H_2O)$_2$] complex

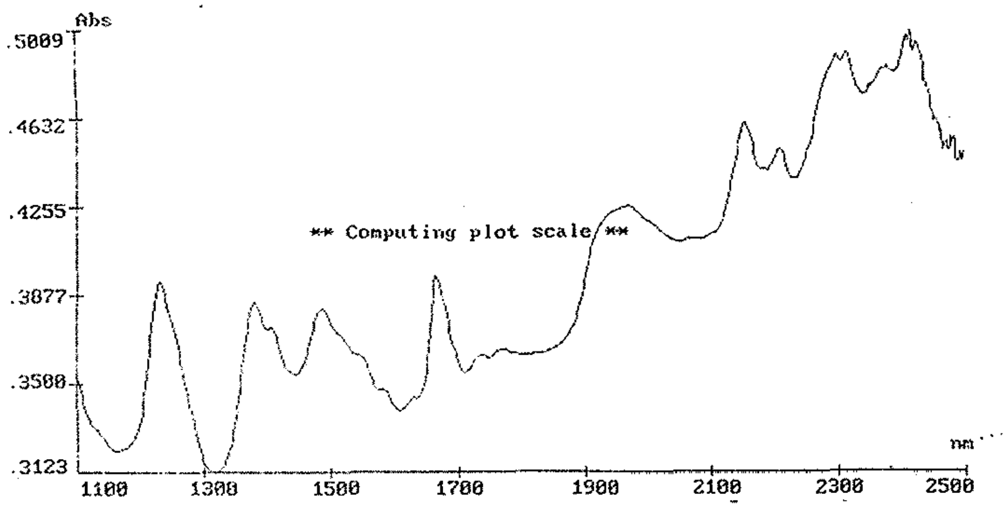


Figure 5. The NIR spectrum of the $K[Sm(L_2)(H_2O)_2]$ complex

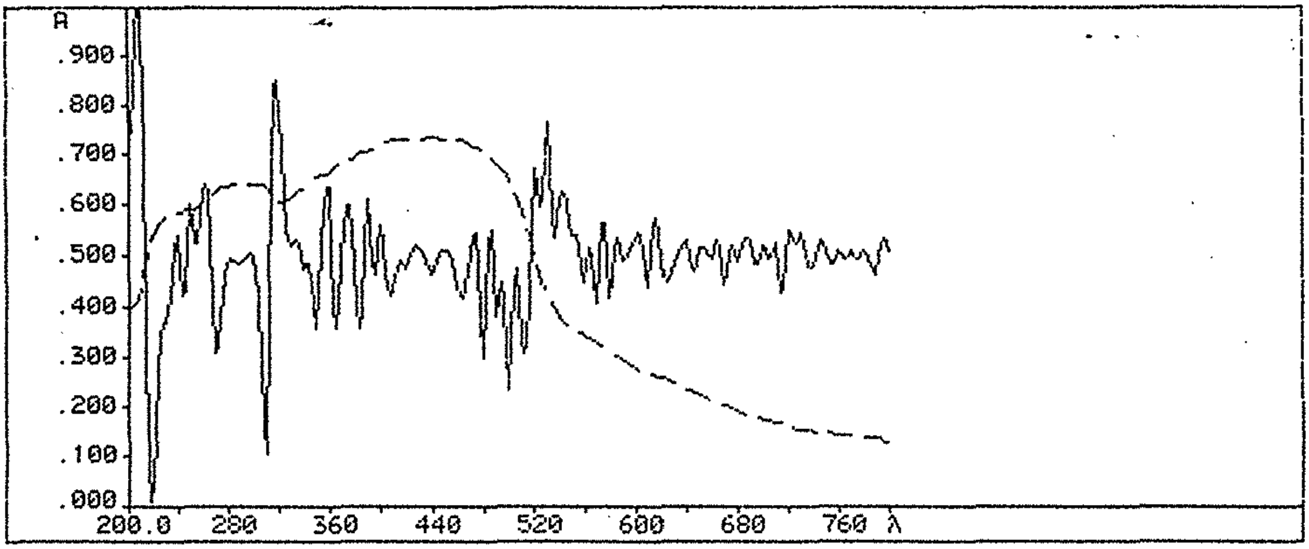


Figure 6. The UV-VIS (nm) spectrum of the $K[Gd(L_2)(H_2O)_2]$ complex

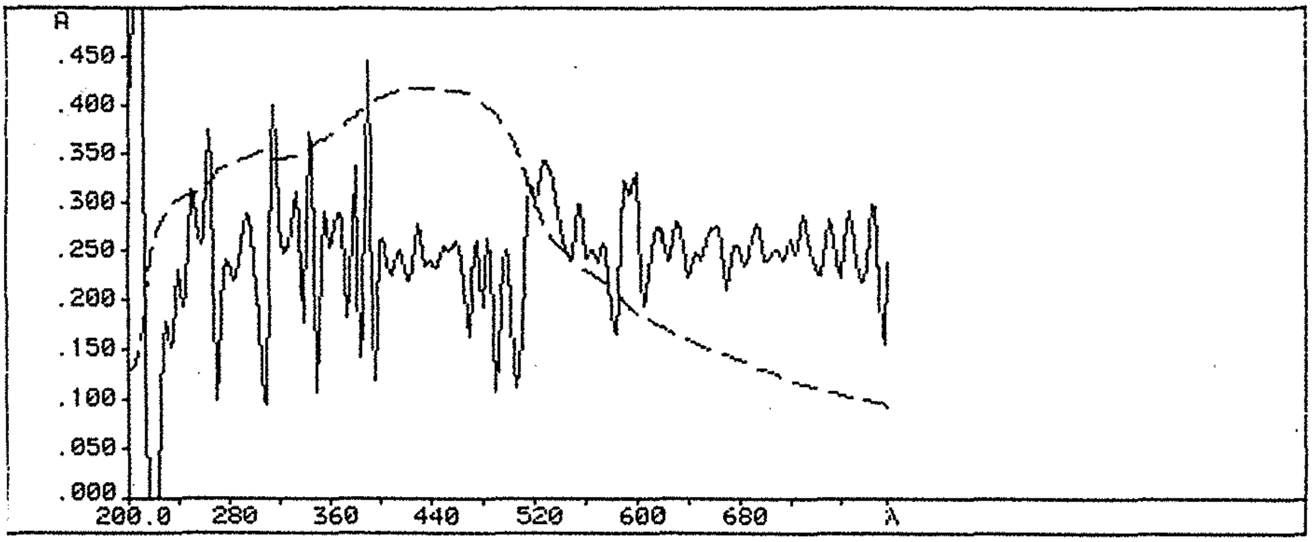


Figure 7. The UV-VIS (nm) spectrum of the $K[Ho(L_2)(H_2O)_2]$ complex

[$GdL_2(H_2O)_2$]. The bands between 32000-33000 cm^{-1} were assigned by Sidall and Stewart[24]. We found three bands in this range assigned to the following transitions:

31250 cm^{-1} for $^8S_{7/2} \rightarrow {}^6P_{7/2}$
32258cm^{-1} for $^8S_{7/2} \rightarrow {}^6P_{5/2}$
32894cm^{-1} for. $^8S_{7/2} \rightarrow {}^6P_{3/2}$

The transitions to ^6I ($^6I_{7/2}$, $^6I_{9/2}$, $^6I_{17/2}$, $^6I_{11/2}$, $^6I_{13/2}$, $^6I_{15/2}$) appear in the range : 36000-37000 cm^{-1}. In our spectrum there is one very intense ligand band at 36340 cm^{-1}, assignedto $^8S_{7/2} \rightarrow {}^6I_{9/2}$. The band at 45454 cm^{-1} was assigned to the transition $^8S_{7/2} \rightarrow {}^6D({}^6D_{9/2,1/2,7/2,3/2,5/2})$. (Figure 6)

[$HoL_2(H_2O)_2$]. In the spectrum of this compound the bands were assigned as follows:

11111cm^{-1}	$^4I_{15/2}$	$\rightarrow {}^5I_5$
16260cm^{-1}		$\rightarrow {}^5F_5$
17094cm^{-1}		$\rightarrow {}^5S_2$
18018cm^{-1}		$\rightarrow {}^5F_4$
19607cm^{-1}		$\rightarrow {}^5F_3$
20000cm^{-1}		$\rightarrow {}^5F_2$
21052cm^{-1}		$\rightarrow {}^3K_8$
23255cm^{-1}		$\rightarrow {}^5G_6$
25000cm^{-1}		$\rightarrow {}^5G_4$
25974cm^{-1}		$\rightarrow {}^3K_7$
28169cm^{-1}		$\rightarrow {}^3G_6$
28985cm^{-1}		$\rightarrow {}^3D_3$
35714cm^{-1}		$\rightarrow ({}^3H_4, {}^5D_4, {}^1G_4)$.[23]

The $^5G_6$ and $^3G_6$ (23255 and 28169 cm^{-1}) are the hypersensitive transitions.
All the band correspond to coordination number eight and a square antiprismatic (C_2) geometry[23,24]. (Figure 7)

References

1.B.B.Mahapatra,D.K.Das,*Acta Chim.Hungaria*,3,124,387-390(1987)
2.A.M.Donia,F.A.El-Saied,*Polyhedron*,7,21,2149-2153(1988)
3.S.L.Stefan,*Microchemical Journal*,35,186-95(1987)
4.C.B.Matho,*J.Chem.Soc.*,LX,917-919(1983)
M.S.Sastry,U.P.Singh,*Synth.React.Inorg.ret.Org.Chem.*,7,24,1213-1225 (1994)
5.A.J.Ryan,S.E.Wright,*Nature (London)*,195,1009(1962)
6. A.J.Ryan,S.E.Wright,*J.Pharm.Pharmacol*,120,291 (1957)
7.P.N.Bangroo,H.C.Arora,*J.Ind.Chem.Soc.*,66,445-447 (1989)
8.Y.Ren,Z.Lin,H.Zhou, *Fenxi Huaxue*, 13,6 (1985)
9.A.A.Kucher,N.S.Poluetkov,*Zavod Lab.*,49,11 (1983)
10.Y.Akame,H.Kanno,*Kidormi*,26,262-3 (1995)
11.A.E.El-Hilaly,N.El-Zamel,*Zh.Neorg.Khim.*,3,40,480-5 (1995)
12.A.Emandi,O.Maior,M.Negoiu,*Rev.Ch.*,3,179-181(1994)
13.W.L.Geary,*Coord.Chem.Rev.*,7,81-87(1971)
14.W.Wang and O.Lin, *Zhougguo Xitu Xuebao*,2,2,1-8 (1984)
15.J.N.Yonathan,*Phys.Chem.Imaging Syst.*,1,157-7 (1994)
16.H.S.Verma and K.C.Mathur, *J.Ind.Chem.Soc.*,LVIII,188 –189 (1981)
17.A.Emandi,D.Negoiu,M.Negoiu,*Anal.Univ.Buc.*,II,19-22 (1993)
18.K.Nakamoto,Ed.,'*'Infrared Spectra of Inorganic and Coordination Compounds*'',J.W.N.Printing Co,Place,(1963),p.158
19.R.C.Aggarwal,R.Bala,R.L.Prasad,*Spectrochim.Acta*,42A,725 (1986)

18.K.Nakamoto,Ed.,' '*Infrared Spectra of Inorganic and Coordination Compounds* '',J.W.N.Printing Co,Place,(1963),p.158

19.R.C.Aggarwal,R.Bala,R.L.Prasad,*Spectrochim.Acta,*42A,725 (1986)

20.B.S.Buyuktas,S.Serin,*Synth.React.Inorg.Chem.Met.Org.Chem.*,7,24,1179-1190 (1994)

21.I.Gamo,*Bull.Chem.Soc.Japan,*34,760 (1961)

22.J.R.Ferrarow,Ed.,' '*Low Frequency Vibration of Inorganic and Coordination Compounds* '',Plenum Press,New York (1973),p.150

23.W.T.Carnall,P.R.Fieldes,*J.Chem.Phys.*,49,4443-4446,(1968)

24.T.H.Siddal,W.E.Stewart,*J.Inorg.Nucl.Chem.*,32,1147-1158(1970)

The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM. http://www.sbjchem.com.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, Nº 6, 1998

SnO_2 - BASED INERT ANODES FOR ALUMINIUM ELECTROLYSIS. THE INFLUENCE OF CeO_2 ADDITION ON THE ELECTRICAL RESISTIVITY.

RODICA GALASIU [1], IOAN GALASIU [1], NICULAE POPA [2], VASILICA CHIVU [2]

[1] INSTITUTE OF PHYSICAL CHEMISTRY
Splaiul Independentei 202, Sector 6, 77 208, Bucharest, ROMANIA
[2] UNIVERSITY OF BUCHAREST, Department of Inorganic Chemistry
Soseaua Panduri 90-92, RO-76235, Bucharest, ROMANIA

ABSTRACT

Five recipes of SnO_2 - based ceramics masses were prepared. The influence of CeO_2 additions on the properties of ceramic masses was studied. It was found that the CeO_2 additions increase the electrical resistivity of these ceramic masses, but the electrical resistivity decreases with the CeO_2 content. The CeO_2 additions have the same influence on the activation energy for conductivity.

RESUMO

Foram preparadas cinco massas cerâmicas baseadas em SnO_2. Foi estudada a influência de CeO_2 sobre as propriedades destas massas. A adição de CeO_2 aumenta a resistividade elétrica, porém esta diminui em função do teor de óxido de cério. As adições de CeO_2 tem a mesma influência sobre a energia de ativação para condutividade.

KEYWORDS: **Inert anodes; aluminium electrolysis.**

DOI: 10.48141/SBJCHEM.v6.n6.1998.65_1998.pdf

1. Introduction

It is very well known that the one of most crucial problems for the use of inert anodes for aluminium production is the slight corrosion resistance of these anodes during the electrolysis in cryolite - alumina melts.

In several papers and patents[1-6] MOLTECH and ELTECH proposed a method to increase the corrosion resistance of these ceramic anodes. This method was used both in the case of the anodes prepared from SnO_2 - based ceramics and in the case of anodes made from cermets. The method consists in introducing a Ce(III) salt in the molten electrolyte. During electrolysis, in the neighbourhood of the anode, the cerium is oxidised and precipitated as an oxifluoride compound deposited like a crust on the anode surface. In this way, a compact layer, adherent to the anode and with a good electronic conductivity is obtained. This layer is protective against the corrosion of molten cryolite.

The ELTECH company tested both in the laboratory and in a pilot plant[5,6] the corrosion resistance of some inert ceramic anodes covered with a protective layer of CeO_2. It was found that the corrosion was reduced about 10 times.

At the cathode in the presence of molten aluminium, the following reaction can occur:

$$CeF_3 + Al = AlF_3 + Ce$$

For this reaction $\Delta G^0 = 259$ kJ/mol, therefore the equilibrium of reaction is removed to the left.

In the present paper are shown results of the electrical resistivity measurements of some ceramic masses: SnO_2 - Sb_2O_3 - CuO - CeO_2 which can be formed on the anode surface during electrolysis.

2. Experimental

The following compositions of SnO_2 - based ceramics masses were prepared:

1. 98% SnO_2 + 2% CeO_2
2. 96% SnO_2 + 2% CuO_2 + 2% CeO_2
3. 95% SnO_2 + 2% SbO_3 + 2% CuO + 1% CeO_2
4. 94% SnO_2 + 2% SbO_3 + 2% CuO + 2% CeO_2
5. 92% SnO_2 + 2% SbO_3 + 2% CuO + 4% CeO_2

These were prepared by mixing the powders in water for 15 hours and then, after drying, by mixing them again with 2 - 3 % polyvinilic alcohol solution, as a binding agent. Pellets having 10 mm in diameter and 3 - 4 mm in height were pressed in a cylindrical mould at 150 atm. The pellets were sintered for 4 hours at 1300°C in an electric furnace. For measuring the electrical resistance of the pellets, they were silver-coated on both sides with silver conducting paste that was then sintered at 700°C. The electrical resistivity of these pellets in direct current was measured. We found that, due to the current passed through it, the pellet gets warmer. For reaching reproducible results, the pellet was thermostated in water at different temperatures.

3. Results and Discussion

The apparent density of the five ceramic masses were measured and the following values were found (Table 1).

The literature[7-10] show that these ceramics have good properties if their apparent density is at least 6.0 g cm^{-3} after sintering. It is noticed from Table 1 that recipe 1, with the composition: 98% SnO_2 + 2% CeO_2 has a very low density, therefore these ceramics are not sintered. The other recipes have good densities, but there is no correlation between the density and the CeO_2 content.

Table 1. Apparent densities of the ceramic masses: SnO_2 - Sb_2O_3 - CuO - CeO_2; t = 20^{0}C.

Recipe	Apparent density (g/cm^3)
1.	4.36
2.	6.12
3.	6.24
4.	6.37
5.	6.34

As shown in our previous paper[11-12] the electrical resistivity of the SnO_2 - based ceramic masses decreases exponentially with increasing current intensity. The same situation was found for the compositions studied in the present paper, as it is seen in Fig. 1 for recipe no. 5. Likewise, Fig. 1 shows that the electrical resistivity decreases with increasing temperature and this fact proves that these ceramics are semiconductors of n type, hence they have an electronic conduction.

The variation of electrical resistivity of the five ceramic masses, studied as a function of the current intensity is given in Fig. 2. The measured surfaces of the pellets were 0.5 - 0.55 cm^2, therefore the current intensities are twice higher. It is noticed that recipe no. 1 has the highest electrical resistivity, but this composition has the lowest density and is not well sintered.

Recipe no. 2, with CuO and CeO_2 as dopant has a lower electrical resistivity. As shown in our previous paper[11-12], the best SnO_2 - based ceramic mass is that which contains 2% SbO_3 and 2% CuO and has the electrical resistivity about 3-10 Ωcm in function of the quality of the raw materials and the sinterization temperature. If to this recipe, 1%, 2% or 4% CeO_2 is added, the ceramic masses no. 3 - 4 - 5 are obtained and their electrical resistivity are shown in figure 2. The CeO_2 addition in any proportion in the ceramic mass 96% SnO_2 + 2% SbO_3 + 2% CuO will increase its electrical resistivity. As seen in Fig. 2, the semiconductor resistivity decreases by CeO_2 concentration increasing.

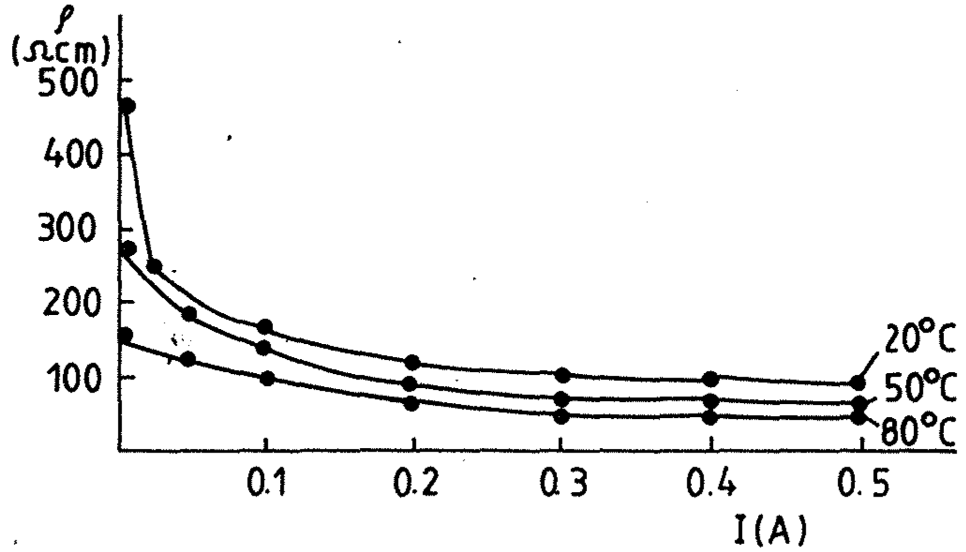


Fig. 1. Variation of the electrical resistivity of the ceramic mass: 92% SnO_2 + 2% SbO_3 + 2% CuO + 4% CeO_2 as a function of the current intensity and temperature.

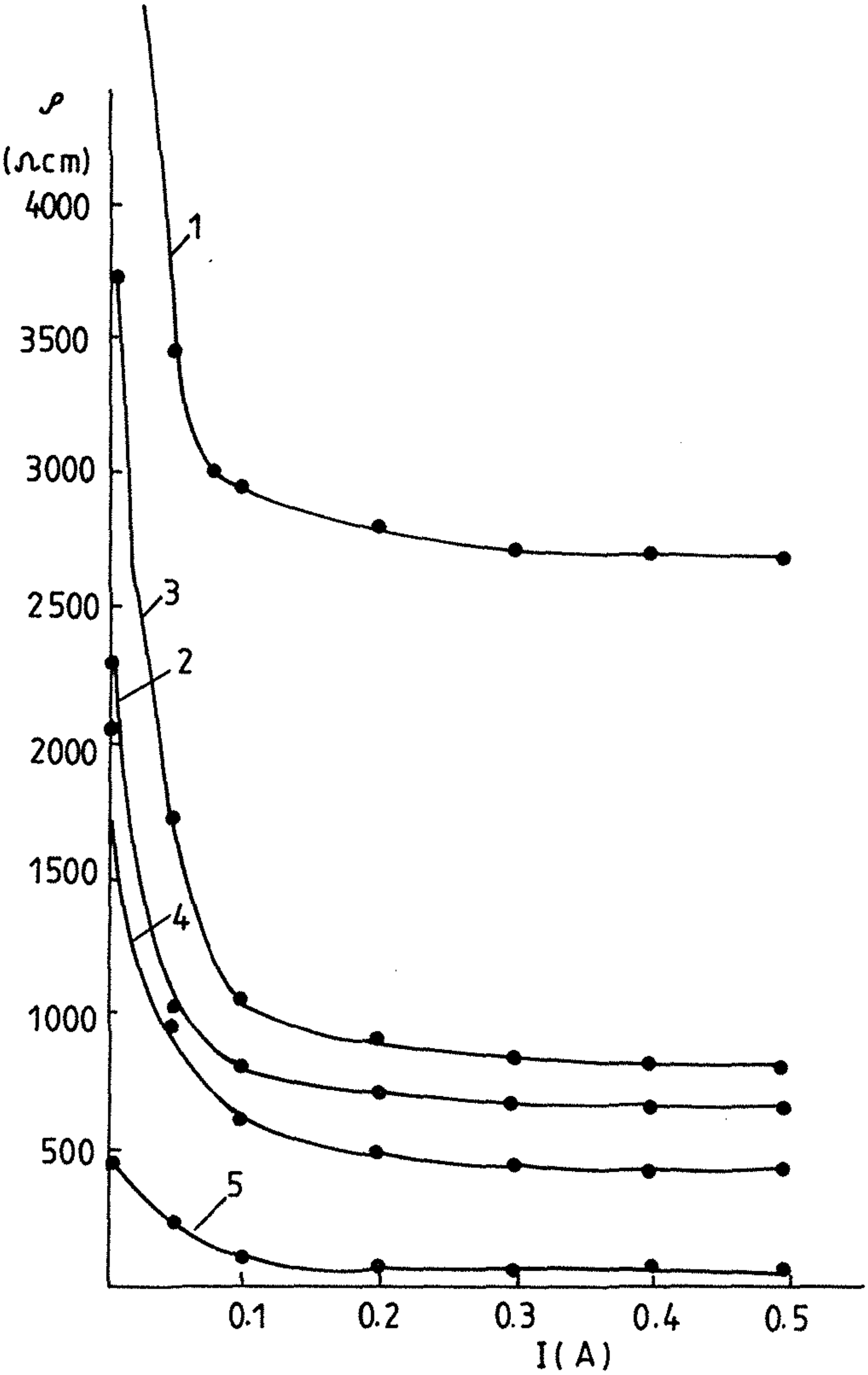


Fig. 2. Variation of the electrical resistivity as a function of the current intensity at $t = 20^0$ C of the ceramic masses with the following composition:

1. 98% SnO_2 + 2% CeO_2
2. 96% SnO_2 + 2% CuO_2 + 2% CeO_2
3. 95% SnO_2 + 2% SbO_3 + 2% CuO + 1% CeO_2
4. 94% SnO_2 + 2% SbO_3 + 2% CuO + 2% CeO_2
5. 92% SnO_2 + 2% SbO_3 + 2% CuO + 4% CeO_2

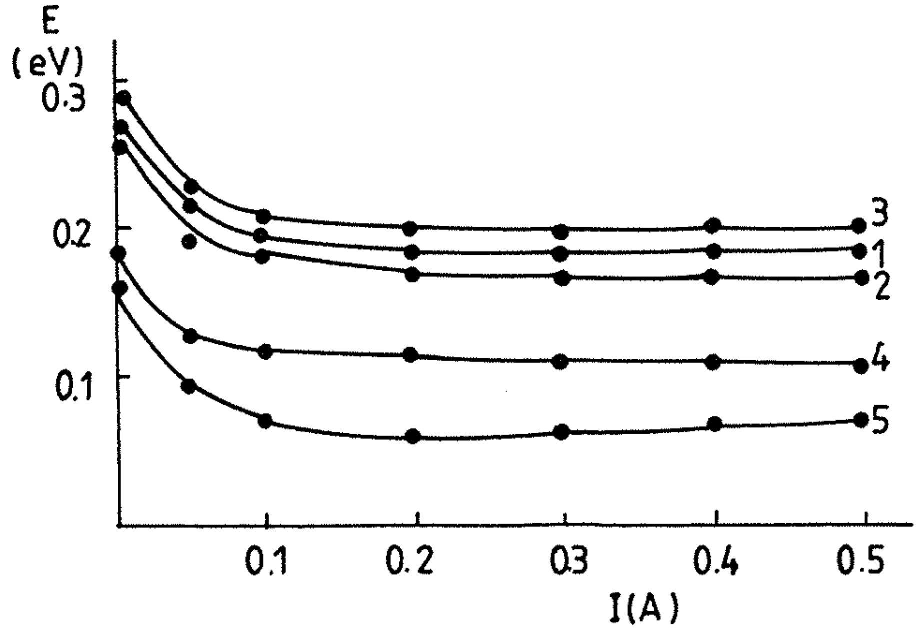


Fig. 3. Variation of the activation energy for electrical conductivity as a function of the current intensity at t = 20^0 C for ceramic masses with the following compositions:

1. 98% SnO_2 + 2% CeO_2
2. 96% SnO_2 + 2% CuO_2 + 2% CeO_2
3. 95% SnO_2 + 2% SbO_3 + 2% CuO + 1% CeO_2
4. 94% SnO_2 + 2% SbO_3 + 2% CuO + 2% CeO_2
5. 92% SnO_2 + 2% SbO_3 + 2% CuO + 4% CeO_2

Based on the electrical resistivity values, the electrical conductivities were calculated, and from the variation with temperature, the activation energies for conductivity were also derived as shown in Fig. 3. A similar variation as with the electrical resistivity was noticed .

If, for the basis recipe: 96% SnO_2 + 2% SbO_3 + 2% CuO, one adds 1%, 2% or 4% CeO_2 ceramic masses were obtained for which the activation energy for conductivity decreases with increasing CeO_2 content. For recipe no. 5, which contains 4% CeO_2, the activation energies are of the same order of magnitude as in the case of the basis recipe: 96% SnO_2 + 2% SbO_3 + 2% CuO[11]. Recipes no. 1 and 2, which contain other compositions, have intermediate values of the activation energy.

4. References

1. J. Bamrochie, Sheriff Robert, (ELTECH Systems Corp.), *Eur. Pat. Appl.* E.P. 257, 709 (Cl.C 25 C 3/12) May 1988.
2. J.K. Walker, J. Kinkoph, C.S. Soha, *J. Appl. Electrochem.*, 19, 225 (1989).
3. ELTECH Systems Corp., *European Patent Specification, 0114.085.B 1* (C25 C 7/02) 1987.
4. J.J. Duruz et al., *U.S. Patent 4*, 614, 569 (Sep. 30, 1986) assigned to MOLTECH Invent S.A.
5. J.S. Gregg, M.S. Frederick, H.L. King, A.J. Vaccaro, *Light Metals*, 1993, p. 445.
6. J.S. Gregg, M.S. Frederick, A.J. Vaccaro, T.R. Alcorn, A.T. Tabereaux, N.E. Richards, *Light Metals*, 1993, p. 465.
7. M. Rolin, J.J. Gallay, *Bull. Soc. Chim. Fr.*, 1960, p. 2093; p. 2096; p. 2101.
8. M. Rolin, *Electrochim. Acta*, 7, 153, (1962).
9. M. Rolin, J. Ducouret, *Bull. Soc. Chim. Fr.*, 1964, p. 790; p. 794.
10. M. Rolin, *Rev. Int. Hautes Temp. Refract.*, 9, 333 (1972).
11. I. Galasiu, R. Galasiu, *Proceedings of the VII Al Symposium*, Donovaly, Slovakia, 1993, p. 57; ibid. p. 69.
12. I. Galasiu, R. Galasiu, E. Andronescu, N. Popa, V. Chivu, *Proceedings of the VIII Al Symposium*, Donovaly, Slovakia, 1995, p. 67.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, N° 6, 1998

EFFECTIVENESS OF CERTAIN STABILIZERS ON THE AGEING OF POLYETHYLENE FILMS

S. JIPA*, R. SETNESCU, T. SETNESCU

Research and Development Institute for Electrical Engineering - ICPE, 313 Splaiul Unirii,
PO Box 104, Bucharest, 74204, Romania

C.PODINA, I.MIHALCEA

University of Bucharest, Faculty of Chemistry, 13 Bd. Carol I,
Bucharest, 70346, Romania

ABSTRACT

The effectiveness of different phenolic antioxidants on high density polyetylene (HDPE) and low density polyetylene (LDPE) has been studied by the isothermal chemiluminescence method. The decreasing order of the antioxidant efficiency for these polymers is as follows:

Irganox 1010 >> Etanox 330 > Irganox 1076 (Hostanox 016) > Topanol OC

RESUMO

Foi estudada a eficiência de vários antioxidantes fenólicos sobre polietileno de alta densidade (PEAD) e polietileno de baixa densidade (PEBD) usando técnicas de quimiluminescência isotérmica. A ordem decrescente de eficiência antioxidante para os dois polímeros foi a seguinte: Irganox 1010 >> Etanox 330 > Irganox 1076 (Hostanox 016) > Topanol OC.

Keywords: polyethylene ; thermal - oxidative destruction ; phenolic antioxidants; chemiluminescence

---

* To whom the correspondence should be addressed

DOI: 10.48141/SBJCHEM.v6.n6.1998.80_1998.pdf

INTRODUCTION

The study of heat stabilization of polyethylene films by commercial antioxidants is not merely of great practical importance but it is also of scientific interest. Extrusion and blowing of polyethylene films expose them to severe degradative conditions, and the need for effective stabilization is therefore an absolute necessity. Stabilizers for this purpose must themselves be heat-resistant and should not sublime or decompose below processing temperature. Approximately 60 antioxidants are marketed in the world for the manufacturing and polyethylene - using industries[1]. The choice of stabilizer for a particular type of polyethylene is governed by the specific nature of the changes which occur in it during the primary working up stage and in storage.

The chemiluminescence (CL) method has be recognised as a useful tool for the evaluation of stabilizers[2-5]. In this work, the CL method was applied to evaluate the thermal oxidative stability of low density polyethylene (LDPE) and high density polyethylene (HDPE), containing certain phenolic antioxidants.

EXPERIMENTAL

Both polyethylene types (films of 0.1 mm thickness) with the characteristics specified in Table 1, were kindly supplied by ARPECHIM Pitesti, Romania.

Table 1. Some characteristics of the polymers studied

Type	Sort	Branching (CH_3 / 1000 C)	Crystallinity (%)	MFI (g / 10 min)	Stabilizer concentration (%)
LDPE	A-2-2-FMA / 002	20	52	0.33	0.02
HDPE	A-5-3-MB / 064	0.5	72	5.09	0.03

The compounds chosen for study were tetrakis (methylene - 3,5 - di - tert - butyl - 4 - hydroxyphenyl) methane propionate (Irganox 1010), 1,3,5 - trimethyl - 2,4,6 - tris (3,5 - di - tert - butyl - 4 - hydroxy benzyl) benzene (Etanox 330), octadecyl - 3 - (3', 5'- di - tert - butyl - 4 hydroxyphenyl) propionate (Irganox 1076 or Hostanox 016) and 2,6 - di - tert - butyl - 4 - methyl phenol (Topanol OC).

Chemiluminescence spectra of the films samples were recorded on a OL - 94 chemiluminescence apparatus manufactured by ICPE, Romania. Chemiluminescence intensity versus time was recorded at constant temperature (190°C) under air flow (1.12 l / min).

RESULTS AND DISCUSSION

Figures 1 and 2 show the chemiluminescence of LDPE and HDPE respectively, both unstabilized and stabilized with the above mentioned antioxidants. As can be seen, some S-shaped CL curves present small shoulders that denote two consecutive antioxidation processes. This observation is in a good agreement with Chien's conclusions[7] about two stages of the decomposition of hydroperoxides in polyethylene.

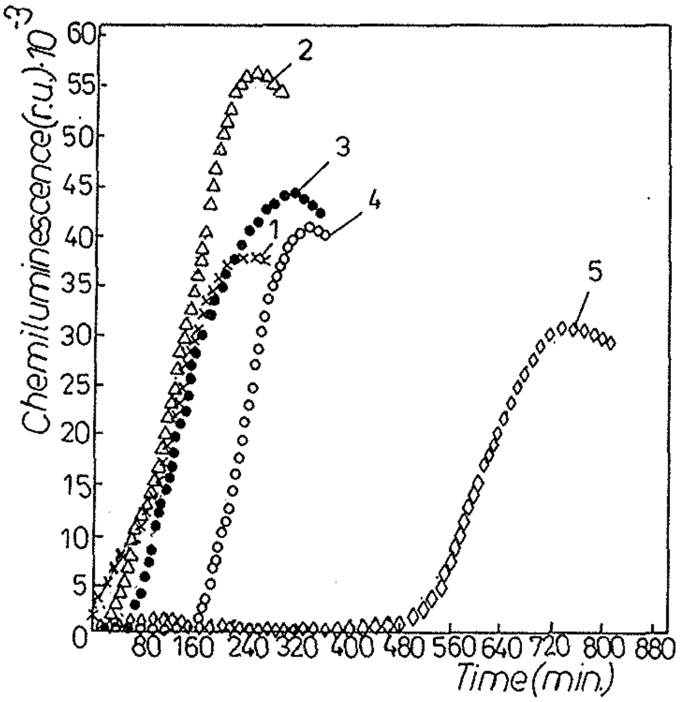


Fig.1. Chemiluminescence intensity as a function of time for oxidation (190°C,air) of LDPE unstabilizerd (1) and stabilized with Topanol OC (2), Irganox 1076 (3), Etanox 330 (4) and Irganox 1010 (5)

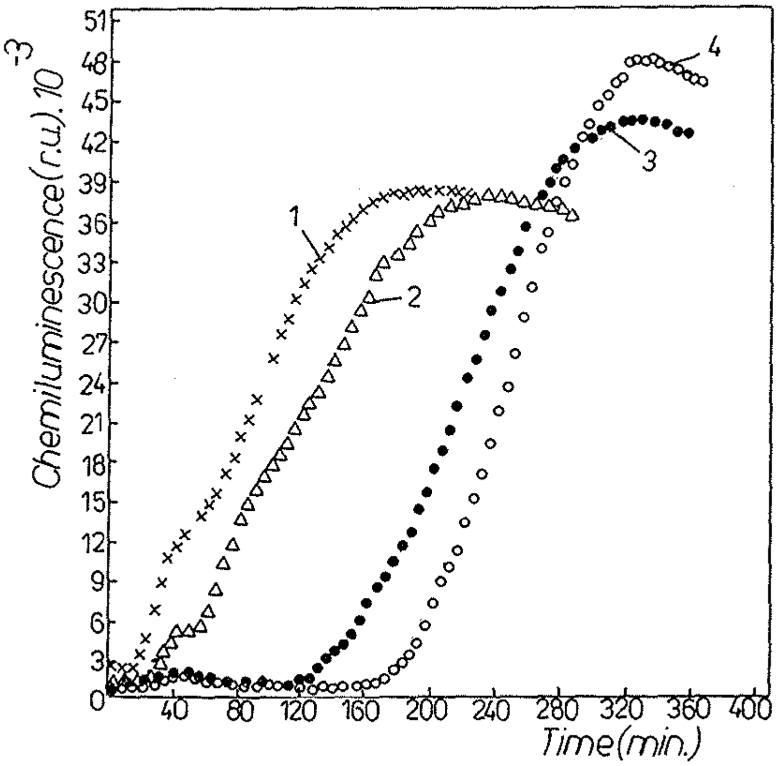


Fig. 2. Chemiluminescence intensity as a function of time for oxidation (190°C, air) of HDPE unstabilized (1) and stabilized with Topanol OC (2), Hostanox 01 (3) and Etanox 330 (4)

Table 2. Values of the kinetic CL parameters (190°C,air) for LDPE and HDPE

	LDPE				HDPE			
Antioxidant	t_i (min.)	V_{ox}^{max} (r.u./min.)	I_{max} (r.u.)	t_{max} (min.)	t_i (min.)	V_{ox}^{max} (r.u. / min.)	I_{max} (r.u.)	t_{max} (min.)
none	19	226	37768	258	28	338	42008	210
Irganox 1010	526	171	30458	765	704	165	28327	900
Etanox 330	185	354	40585	345	192	477	48039	340
Irganox 1076 or Hostanox 016	71	311	44236	315	155	370	43443	330
Topanol OC	52	302	55903	259	43	384	37601	236

The kinetic analysis of chemiluminescence data was made using the following parameters (Table 2): the induction period (t_i), the maximum oxidation rate (V_{ox}^{max}), the CL emission maximum intensity (I_{max}) and the time for reaching the CL maximum emission value (t_{max}).

Table 3. The antioxidant effectiveness parameters for LDPE and HDPE (190°C,air)

Antioxidant	LDPE		HDPE	
	A	S	A	S
Irganox 1010	15.4	0.76	45.1	0.49
Etanox 330	5.0	1.57	10.9	1.41
Irganox 1076 or Hostanox 016	1.6	1.38	8.5	1.09
Topanol OC	1.0	1.34	1.0	1.14

Table 3 shows the antioxidant activity (A) expressed by the relation[8,9]:

$$A = (t_x - t_0) / (t_s - t_0)$$

where t_0, t_x and t_s are, respectively, the induction periods graphically deduced from chemiluminograms for pure polymer, for polymer with the particular antioxidant and with Topanol OC, which was taken as a standard.

The relative stability (S) was calculated using the following relation[8]:

$$S = (V_{ox})_x / (V_{ox})_0$$

where $(V_{ox})_0$ and $(V_{ox})_x$ are the maximum oxidation rate for pure and antioxidant - protected polymer, respectively. This parameter is also given in Table 3.

As can be seen, all stabilizers studied inhibited LDPE and HDPE degradation in air at 190°C by trapping the radicals formed in the matrix. This is confirmed by the increased values of the time parameters t_i and t_{max} in comparison to the blank sample. The V_{ox}^{max} parameter decreased only slightly , due to the high temperature of the oxidation reaction, when the most analysed antioxidants cannot be active after the induction period has ceased. A similar trend was observed for I_{max} parameter.

The product Irganox 1010 exhibits the highest protection capability among the antioxidant studied. For this antioxidant the highest increase in the length of the induction period was obtained and the lowest V_{ox}^{max} parameter was recorded. This means that the oxidation products of Irganox 1010 are still able to participate as protecting agents in the propagation period. This is also proved by the lowest I_{max} value recorded in the case of this stabilizer (i.e. minimum quantities of hydroperoxide are formed).

On the other hand, as can be seen in Table 3, the antioxidant efficiencies for HDPE samples were much higher than that for LDPE ones. Judging from the time chemiluminescence parameters the decreasing order of the antioxidant efficiency in both polymers is as follows;

Irganox 1010 >> Etanox 330 > Irganox 1076 (Hostanox 016) > Topanol OC

This antioxidant ranking is in a good agreement with the order obtained by the other methods[10-12]. This fact apparently indicates that the isothermal chemiluminescence method can be used for evaluating of thermal oxidative stability of the polyolefinic films. One of the advantages is that only a very small amount (ca. 35 mg) is required for the measurement of the chemiluminescence.

REFERENCES

1. S.Horun and O.Sebe, *Degradarea si stabilizarea polimerilor*, Editura Tehnica, Bucuresti, 1983, pp. 394 - 420.
2. L.M.Rychla, Z.Fodor and J.Rychly, *Polym.Degrad.Stab. 3*, 371 - 382 (1981)
3. L.Zlatkevich, *J. Polym. Sci. Polym. Lett. 21*, 571 - 574 (1983)
4. Z.Osawa and K.Tsurumi, *Polym.Degrad.Stab. 26*, 151 - 160 (1989)
5. S.Jipa, T.Setnescu, R.Setnescu, C.Cazac and I.Mihalcea, *Chem.Rev (Bucharest), 44*, 65 - 70 (1993)
6. S.Jipa, Z.Osawa, H.Otsuki and M.Nishimoto, *Polym.Degrad.Stab. 56*, 45-53 (1997)
7. J.C.W.Chien, *J.Polym.Sci. A - 1, 6*, 375 -379 (1968)
8. L.Jirakova and J. Pospisil, *J.Eur.Polym. 9*, 71 - 76 (1973)
9. L.Jirakova and J. Pospisil, *Coll. Czech. Chem. Commun. 40*, 2800 -2805 (1975)
10. N.S.Allen, A.Hamidi A., D.A.R.Williams, F.F. Loffelmann, P.MacDonald and P.V.Sussi, *Plast.Rubb.Process.Appl. 6*, 109 - 114 (1986)
11. C.Andrei and P.Ioana, *Chem.Rev. (Bucharest) 39*, 1068 - 1072 (1988)
12. S.Jipa, R.Setnescu, T.Setnescu, C.Cazac,P.Budrugeac and I. Mihalcea, *Polym.Degrad. Stab. 40*, 101 -107 (1993)

The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM. http://www.sbjchem.com.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, Nº 6, 1998

IMMOBILIZATION OF ALCOHOL OXIDASE IN SIO_2 MATRIX PREPARED BY SOL-GEL METHOD

Lia Stanciu, Melania-Liliana Arsene[a] and Constanta Parlog

Institute of Physical Chemistry "I.G. Murgulescu" of Romanian Academy,
Spl. Independenței 202, Bucharest 77208, Romania
[a] *Department of Biotechnology, Chemical Research Institute, Spl. Independentei 202, 77208,*
Bucharest, Romania

ABSTRACT

The possibility of obtaining a biochemical sensor for colorimetric determination was studied. For this purpose, we have used the redox indicator 2,6- dichlorophenolindophenol (DCIP) and the binary enzymatic system composed by alcohol oxidase (AO) and peroxidase (PER). The binary enzymatic system immobilized in an inert SiO_2 matrix was obtained by modified sol-gel process. The chromogen and binary enzymatic system immobilization into a SiO_2 matrix was confirmed by I.R. spectroscopy. By immobilization of the enzymatic system, both the stability and enzymatic activity increase.

KEYWORDS sol-gel, immobilization, enzymes, alcohol oxidase, 2,6-dichlorophenolindophenol

RESUMO

Foi estudada a possibilidade de obter um sensor para determinações colorimétricas. Para isso foi usado indicador 2,6-diclorofenolindofenol (DCIP) e o sistema enzimático binário consistindo de alcool oxidase (AO) e peroxidase (PER). O sistema binário enzimático foi imobilizado numa matriz inerte de SiO_2 usando um método modificado sol-gel. A imobilização do cromogênio e do sistema enzimático binário foi confirmada através de espectroscopia no infravermelho.
A imobilização do sistema enzimático leva a uma aumento de estabilidade e da atividade enzimática.

DOI: 10.48141/SBJCHEM.v6.n6.1998.86_1998.pdf

1. Introduction

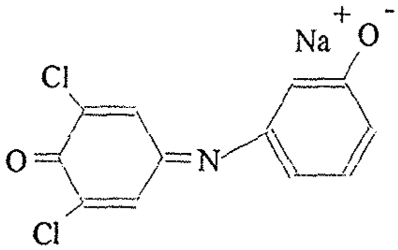
The studies of biochemical sensors based on immobilization of enzymes have lately shown a rapid development The biosensors enjoy a wide application and offer considerable advantages in industry, protection of the environment and medicine [1]. Among the advantages utilization of biosensors ensure in analytical chemistry one should mention the smaller amount of chemicals employed and more facile preparation of samples.

Different methods have been employed to obtain stable operational biosensors to be used in quantitative analysis of some chemical species such as utilization of enzymes originating in thermally stable bacteria or addition of stabilizing compounds to original enzymes. Studies have shown that addition of electrochemical compounds mixed with polyhydroxylic solutions to the enzyme confer them a high thermal stability in a dehydrated state as well as in solution. The mechanism of enzyme stabilization involves the formation of an electrostatic cage around the enzyme, resulting in an enzyme – polyelectrolyte complex which retains the enzyme in a more rigid configuration [2]. The most important characteristic of the biosensors is their selectivity. The preparation of a new biosensor usually aims to radically change the analytical characteristics increasing the ability to determine wider variety of compounds and also the selectivity in the detection of each specific compound. The main factors [3] which determine the selectivity of the biosensors are:

- the nature of the biomaterial;
- the method of biospecific preparation (the type of immobilization and purification, choice of inert matrix for immobilization, biomaterial treatment by specific effectors etc.);
- the characteristics of the analytical detector and the specialties of its combination with the biospecific preparation;
- the conditions of biospecific reactions unfolding (sample composition, temperature).

Operation of electrochemical biosensors requires a conjugation of biochemical and electrochemical reactions. The biological recognition element should be immobilized at the electrode surface. There are two principal ways to do such an immobilization: covalent linking and the entrapment into gel or polymer matrix [4]. Besides the electrochemical biosensors used for amperometric determinations, biosensors used for colorimetric determinations have been also obtained and studied. In both cases, an important feature is the enzyme immobilization in an inert matrix [5].

This contribution aims to obtain biosensors based on alcohol oxidase (AO), using 2,6-dichlorophenolindophenol (DCIP) as redox indicator.



Chemical structure of DCIP (2,6- dichlorophenolindophenol)

This investigation intends to determine the optimal conditions required for immobilization and stabilization of AO+PER type binary system, of redox indicator(DCIP) and finally the immobilization of the whole enzymatic system (alcohol oxidase (AO)+peroxidase (PER) + redox indicator (DCIP)) in a SiO_2 inert matrix prepared by the sol-gel method. The influence of the alkoxide, solvent, catalysis type and hydrolysis ratio upon the catalytic activity of the selected enzymatic system are also studied.

2.Experimental

The (AO + PER + DCIP) enzymatic system was selected to obtain a biosensor based on colorimetric determination to be employed in detecting alcohol traces.

The unfolding of the process involves the following steps:

- the redox indicator (DCIP) immobilization in a SiO_2 matrix prepared by a sol-gel method;
- immobilization of alcohol oxidase (AO) in inert SiO_2 matrix;
- immobilization of the whole (AO + PER + DCIP) enzymatic system in SiO_2 matrix prepared by the sol-gel method.

The sol was obtained from the following components: tetraethoxysilane alkoxide; 2-methyl – 1 – propanol (1-isobutanol) as a solvent. The basic catalysis employed NH_4OH as catalyst.

The conditions of inclusion and immobilization of the enzymatic system in the silica gel are listed in Tables 1 and 2. All reactions were carried out in alkaline catalyzed sols, at pH ranging between 8 and 9.

Incorporation and immobilization of the selected enzymatic system into the silica gel were monitored by IR spectroscopy.

The qualitative test employed to determine the activity of alcohol oxidase immobilized in SiO_2 gel was carried out as follows : 0.1 mL of concentrated peroxidase and chromogenic reagent (DCIP) and 0.03 mL of substrate (95%

ethanol), over 0.5 cm^2 surface area of SiO_2-containing AO was poured, as uniformly as possible.

In case when AO, as well as PER and DCIP were immobilized, the qualitative determination of the enzymatic activity was done by uniform drop wise addition of the substrate only on gel surface. In both cases, the enzymatic reaction was evaluated by visualizing the changes of the color DCIP redox indicator.

3. Results and Discussions

Immobilization of DCIP redox indicator

The preparation of a colorimetric biosensor requires utilization of a chromogen in the enzymatic system which has to fulfill two basic conditions: (i) colorimetric difference between the reduced and oxidized forms;(ii) low electrochemical potential which should be correlated with that of the enzymatic reaction.

In this contribution, we have used DCIP as chromogen indicator , since its redox potential (+ 0.23) is adequate for the alcohol oxidase--peroxidase binary enzymatic system. At the same time it is characterized by a net difference between the colors which correspond to both oxidation states: $DCIP_{red}$ (leucoform) and $DCIP_{ox}$ (blue form). This redox indicator may be employed in the enzymatic reaction in the reduced as well as in the oxidized state; in the latter the DCIP decomposition ($DCIP_{decom}$) reaction occurs(pale mauve form).

The low electrochemical potential of the redox indicator employed in the enzymatic reaction represents a draw back from the point of view of indicator stability. Thus, regardless of the chromogen form which is accessible in the enzymatic reaction, it is susceptible to chemical oxidation produced by the action of oxygen in solution or in the atmosphere this influences the biosensor's activity. Under these circumstances, a first step in obtaining an alcohol oxidase--based biochemical sensor with colorimetric determination requires the testing of the stability of DCIP immobilized in the inert silica matrix .

Comparison of the reduced stability of the both DCIP forms in aqueous solution at room temperature (maximum two days),shows that their immobilization in SiO_2 matrix increases significantly the stability to 60-70 days (Table 1).

Table 1. Experimental conditions of *2,6- dichlorophenolindophenol* (DCIP) immobilization in the sol-gel silica

No. Sol.	i-BuOH/TEOS	H_2O/TEOS	$DCIP_{OX}$/TEOS	$DCIP_{RED}$/TEOS	Time Activity (days)
1	2.5	6.25	$5.7 \cdot 10^{-6}$	$5.7 \cdot 10^{-6}$	60
2	2.5	6.25	$2.9 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	60
3	7.5	1.25	$5.7\ 10^{-6}$	$5.7\ 10^{-6}$	70
4	7.5	1.25	$2.9\ 10^{-5}$	$2.9\ 10^{-5}$	70
5	5.0	2.5	$5.7\ 10^{-6}$	$5.7\ 10^{-6}$	65
6	6.2	3.12	$2.8\ 10^{-6}$	$2.8\ 10^{-6}$	65
7	-	1.53	$3.4\ 10^{-7}$	$3.4\ 10^{-7}$	70

*The ratios in the table are molar ratios

DCIP - 2,6- dichlorophenolindophenol
TEOS - tetraethoxysilane
i-BuOH – iso-butanol

Immobilization of Alcohol Oxidase

The obtention of the matrix combination by the sol-gel requires two important steps: transition from sol to gel and transition from gel to finite product (film, powder or ceramic).

Schematically, such a process consists in the following important steps:

$$\text{Precursor} \xrightarrow{\text{Hidrolysis}} \text{Reactive monomer} \xrightarrow{\text{Condensation}} \text{Sol} \xrightarrow{\text{Gelation}} \text{Gel}$$

Because sol-gel transition takes a relatively long time (10-12 days), compared to the lifetime of enzyme in aqueous solution at the room temperature, one resorts to utilization of a small quantity of water and to the delayed introduction of alcohol oxidase in the silica sol, such that the inactivation process is reduced or even eliminated.

The AO was added 10-11days after the start of the hydrolysis-polycondensation reaction and the gelation occurred in 25-30 minutes. If the enzyme is maintained for the shortest time in aqueous solution one avoids the denaturation and the loss of catalytic activity due to the operational instability of the enzyme in aqueous medium..

Methanol is the main substrate of the alcohol oxidase oxidation reaction, but the enzyme does not possess an absolute substrate specificity. It can also catalyze oxidation reactions of lower alcohols with a reduced number of carbon atoms and a linear chain, such as ethanol. Therefore utilization of this solvent to obtain SiO_2 sols was avoided ; ethanol was replaced by iso-butanol , a four carbon atom alcohol with branched chain, less accessible for the enzyme, but equally efficient from the viewpoint of silica sol preparation.

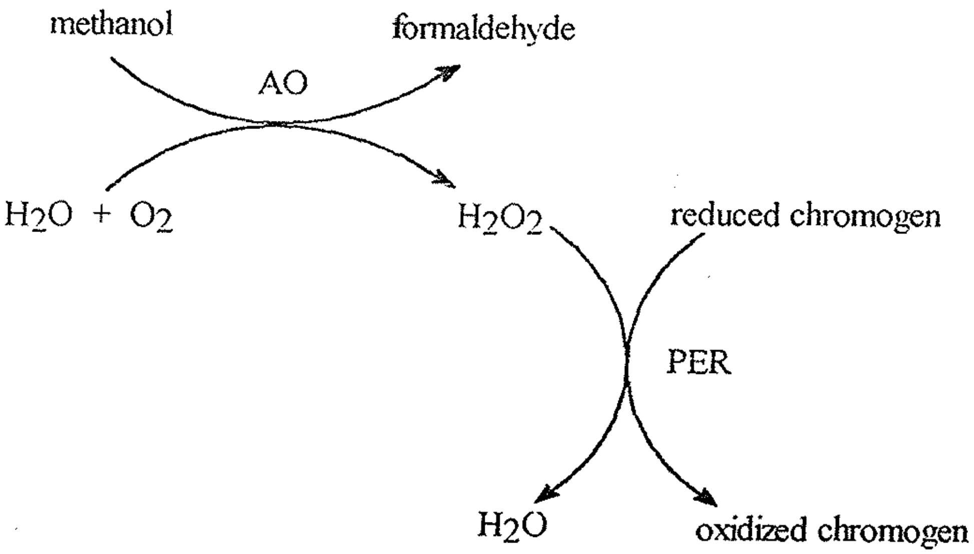
However, small amounts of ethanol resulted from the basic reaction used to obtain the silica matrix by hydrolysis reaction. The slowing down of the hydrolysis reaction by employing a small hydrolysis ratio, modification of the solvent nature and delaying of the introduction of the enzyme in the system offer the advantage of eliminating ethyl alcohol traces by evaporation.

Immobilization of AO + PER + DCIP enzymatic system

A biosensor was developed, which is utilized in colorimetric measurements employing alcohol oxidase as biochemical product. The colorimetric dosage of alcohol oxidase activity in aqueous medium is based on determining one of the products of methanol oxidation reaction, i.e. hydrogen peroxide, by coupling the first enzymatic reaction with the second enzymatic system: peroxidase-chromogen (DCIP). The hydrogen peroxide resulting from the main reaction forms a strongly oxidizing complex with peroxidase, which will oxidize the chromogen according to Scheme 1.

The immobilization and stabilization of the complex enzyme system consisting of the mixing all compounds that are the alcohol oxidase, the peroxidase and the redox indicator (2,6 dichlorophenolindophenol) was obtained under similar conditions with inclusion of simple alcohol oxidase into the silica matrix. The experimental conditions are listed in Table 2.

. The immobilization of AO+PER enzymatic system and DCIP redox indicator in the silica matrix was evidenced by IR spectroscopy. Therefore the IR spectra of the pure SiO_2 gel and of samples SiO_2+PER and SiO_2+AO+DCIP were recorded in the 4000-400 cm^{-1} range.



Scheme 1. Diagram of alcohol oxidase activity determination

AO – alcohol oxidase; PER - peroxidase

Table 2. The experimental conditions for immobilization of alcohol oxidase (AO) + peroxidase (PER) + 2,6- dichlorophenolindophenol (DCIP) enzymatic system in the silica matrix obtained by sol-gel method.

No. sol	pH	AO (mU)	PER (U)	DCIP (μmoli)	Gelation time (minutes)	Time activity (days)
1	8	1	8	0,25	30	70
2	9	5	40	0,25	25	65
3	8	10	80	0,25	20	60

The bands assigned to Si-O vibration bonds in SiO_2 are present in all spectra within the wavelength number 400-500, 800-900 and 1000-1100 cm^{-1} as can be seen in Figure 1 [6].

The redox indicator DCIP presence is illustrated by the existence of the specific bands in the range 600-800 cm^{-1} (Figure 1c). The inclusion of the enzymes in the silica matrix is suggested by the splitting of the bands around 1600 cm^{-1} which are assigned to C=O and N-H enzymes vibrations . On the other hand, the strong band at 1370-1380 cm^{-1} noted in the spectra shown in Figures 1b and 1c was assigned to the enzyme carboxylate ion symmetric vibration of υ_{symCOO^-}.

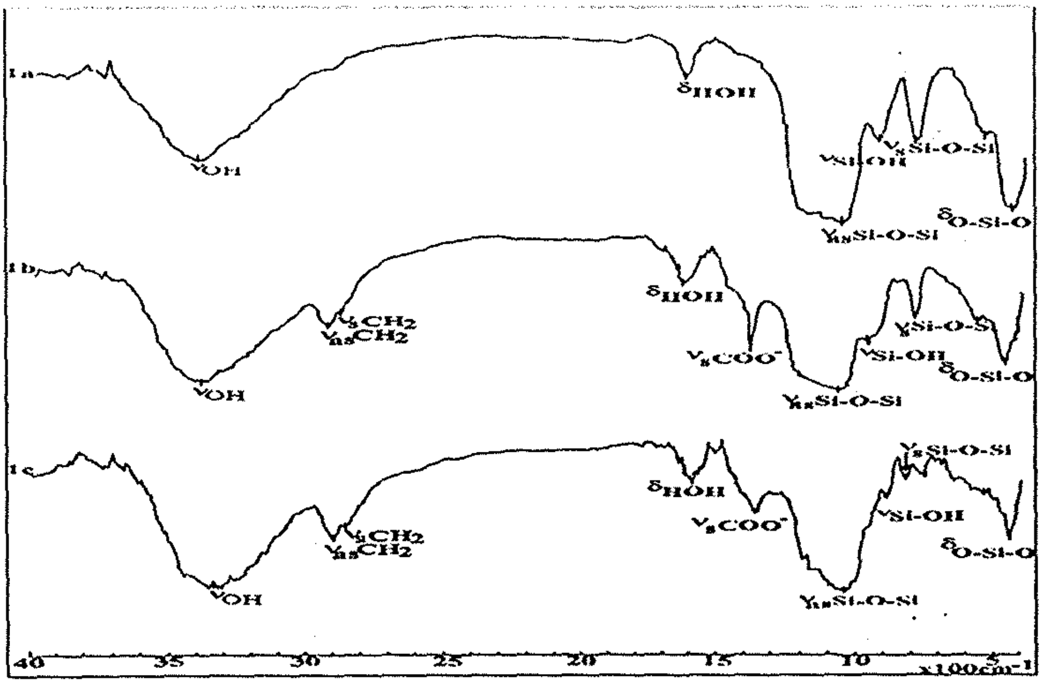


Figure 1. Infrared spectra of the pure SiO_2(a), SiO_2 doped with peroxidase(b) and SiO_2 doped with alcohol oxidase and 2,6- dichlorophenolindophenol (c)

The general aspect of higher splitting of the bands in the spectrum was assigned to the larger volume of the alcohol oxidase which induced perturbation in the molecular symmetry (Figure 1c).

The structure of SiO_2 gel is favored by peroxidase , a bulkier enzyme (Figure 1b). The band at 800 cm^{-1},assigned to symmetric vibration $\upsilon_{symSi\text{-}O\text{-}Si}$ is present in the spectrum 1b and it miss from the spectrum 1c.

The evaluation of IR spectra suggests that the enzymes (AO and PER) and the redox indicator (DCIP) were successfully immobilized in silica gel. Besides one may conclude that the inclusion and immobilization of peroxidase affects to a lesser extent the structure of the SiO_2 matrix.

Catalytic activity of the AO+PER+DCIP enzymatic system

Besides immobilization and stabilization of the selected enzymatic system, in an inert silica matrix prepared by sol-gel method, we attempted to uncover the conditions which preserve the catalytic activity of the enzyme. This is conditioned by the retaining of enzyme molecule quaternary structure. The activity of alcohol oxidase molecule, whose size is 12x12x12 nm, is ensured by the eight identical subunits (molecular weight amounts to 80000 Dalton per monomer); the subunits are bonded by 2-3 FAD (flavine adenine dinucleotide) molecules [7].

Immobilization and stabilization of alcohol oxidase in silica matrix prepared by sol-gel method was optimal from the viewpoint of catalytic activity which suggest that the oligomer structure of the enzyme remained unchange. The monomers unbounded to FAD are inactive from the enzymatic viewpoint. Retaining the catalytic activity of the alcohol oxidase was carried out by separate immobilizing of the alcohol oxidase as well as immobilizing the whole(AO+PER+DCIP). enzymatic system.

4. Conclusions

Immobilization has significantly increased the redox indicator, DCIP, time stability in reduced as well as in oxidized form compared to aqueous medium.

The sol-gel method of preparing the inert inorganic SiO_2 matrix was adapted to alcohol oxidase characteristics (stability in aqueous solution, substrate specificity) by establishing the hydrolysis ratio, the change of solvent and establishing the adequate time when the enzymatic system is introduced.

The immobilization of chromogen DCIP and of AO+PER enzymatic system in silica matrix was confirmed.

The possibility of immobilizing a AO+PER binary system into silica gel, retaining the catalytic activity of the enzyme was outlined;

The possibility to obtain, for the first time in our country, a biochemical sensor for colorimetric determination was studied. Use has been made of DCIP redox indicator and of the enzymatic binary AO+PER system immobilized in a SiO_2 inert matrix prepared by sol-gel matrix to detect traces of lower alcohol (methanol or ethanol).

References

1.E.P. Medyantseva, H.C. Bucnikov, M.P. Kutireva, M.G. Vertlib, S.S. Babkina, *Eurosensors X*, **1996**, 941-943;

2. B. Appleton and T.D. Gibson, *Eurosensors X*, **1996**, 83-85;

3.O.V. Yagodina, E.B. Nikolskaya, *Eurosensors X*, **1996**, 929-932;

4.Lylia V. Lukachova, Arkady A. Karyakin, Elena E. Karyakina, Lo Gorton, *Eurosensors X*, **1996**, 75-78;

5. Jeffrey I. Zink, Stacey A. Yamanaka, Lisa M. Ellerby, Joan S. Valentine, Fumito Nishida and Bruce Dunn, *J. Sol-Gel Sci. Technol*, **1994**, 791-795;

6. Yoshiro Tatsu, Keishi Yamashita, Muneaki Yamaguchi, Soichiro Yamamura, Hitoshi Yamamoto and Susumu Yoshikawa, *Chemistry Letters*, **1992**, 1615-1618;

7. N.Kato, Y.Omori, Y.Tani and K.Ogata, *Eur.J.Biochem.*, **1976**, 341-345

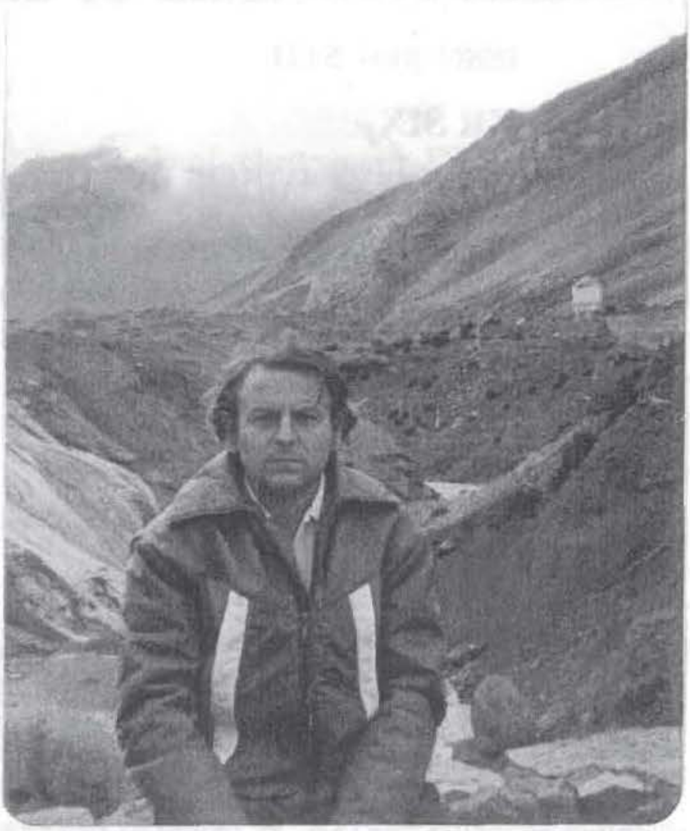
SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

ISSN 0104-5431

VOLUME SIX, NUMBER SIX JULY 1998

AUTHOR INDEX / ÍNDICE DE AUTORES

Arsene, Melania Liliana 77
Balasoiu, Mariana 53
Calistru, Maria 33
Chivu, Vasilica 63
Crocnan, D. 25
Emandi, Anca 53
Galasiu, Ion 63
Galasiu, Rodica 63
Gavriloaiei, T. 33
Greabu, Maria 25
Jipa, S. 71
Kid, B. J. 1
Kummerow, E. A. 25
Martinez, A. D. 1
Migliavacca, Daniela Montanari 11
Mihalcea, I. 71
Mocanu, Raluca 33
Olariu, R. 33
Olinescu, R. M. 25
Parlog, Constanta 77
Paveliu, Fraga 25
Podina, C. 71
Polli, Vania Regina Gabbi 45
Popa, Niculae 63
Prochnow, Alnei Ramos 45
Rosu, Tudor 53
Sanchez, Josete Dani 11
Setnescu, R. 71
Setnescu, T. 71
Stanciu, Lia 77
Tamanini, Juliane Zimmerman 45
Teixeira, Elba Calesso 11

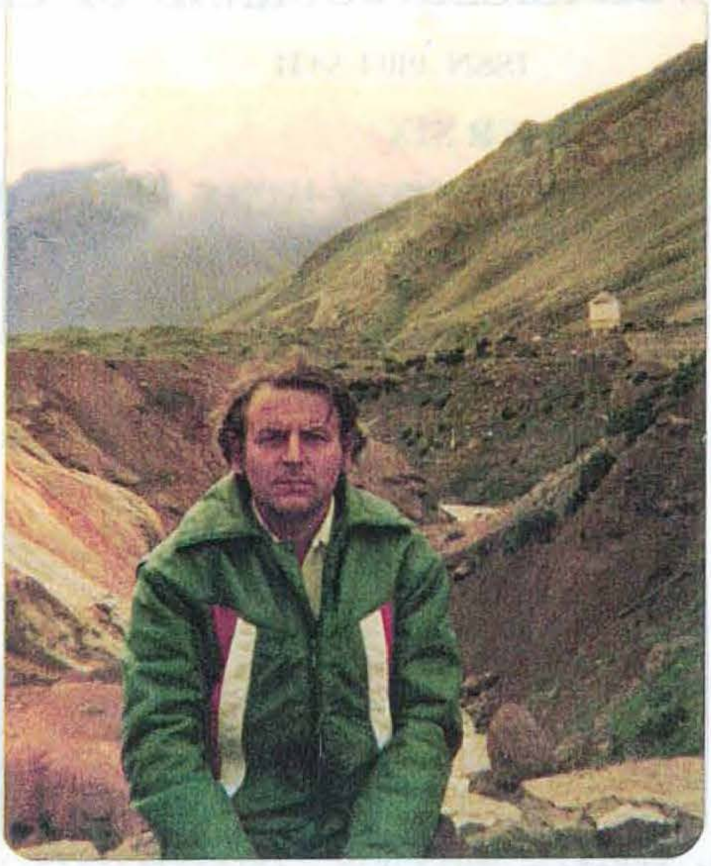


AT THE FEET OF ACONCAGUA, PUENTE DEL INCA,
PROVINICIA DE MENDOZA, REPUBLICA ARGENTINA.

ACONCAGUA, SOUTH AMERICA'S HIGHEST PEAK IN THE CORDILLERA OF THE ANDES (6958 or 7035m).

AT THE FEET OF ACONCAGUA, PUENTE DEL INCA, PROVINICIA DE MENDOZA, REPUBLICA ARGENTINA.

ACONCAGUA, SOUTH AMERICA'S HIGHEST PEAK IN THE CORDILLERA OF THE ANDES (6958 or 7035m).



AT THE FEET OF ACONCAGUA, PUENTE DEL INCA,
PROVINICIA DE MENDOZA, REPUBLICA ARGENTINA.

ACONCAGUA, SOUTH AMERICA'S HIGHEST PEAK IN THE CORDILLERA OF THE ANDES (6958 or 7035m).

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

ISSN 0104-5431

The *SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY* is an international forum for the rapid publication of original scientific articles dealing with chemistry and related areas. At the present there are no page charges and the authors will receive twenty five free reprints of their papers.

SPECIAL COMBINATION OFFER FOR NEW SUBSCRIBERS!

SUBSCRIPTION INFORMATION

PRICE: Brazil and Latin America: US$ 35.00 per issue.

Other Countries: US$ 50.00 per issue, including air mail delivery.

Persons or institutions outside Brazil should send subscription fee payable to Dr. L. G. Ionescu, c/o SBJC
8532 Howard Circle, Huntington Beach, California, USA
92647

ORDER FORM

☐ Please enter my subscription for _______ issues of Southern Brazilian Journal of Chemistry.

☐ Please send me _____ copies of the Southern Brazilian Journal of Chemistry Vol. 1,2,3,4,5,6 (1993-1998) (Circle desired copies.)

☐ I enclose a check or money order in the amount of $_______

☐ Please send me a Pro Forma Invoice for the above order.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

Lavinel G. Ionescu, B.S., M.S., Ph.D., Editor
Caixa Postal 15032, Agronomia
Porto Alegre, RS BRASIL 91501-970

TEL. 55 51 485-1820 FAX 55 51 320-3612 or 55 51 477-1313

EMail: LGIPUCRS @ MUSIC.PUCRS.BR
LAVINEL @ MOZART.ULBRA.TCHE.BR

INFORMATION FOR AUTHORS

The Southern Brazilian Journal of Chemistry - SBJC will publish review articles, original research papers and short communications dealing with chemistry and interdisciplinary areas such as materials science, biotechnology, bioengineering and other multidisciplinary fields.

Articles report the results of a complete study. They should include an Abstract, Introduction describing the known art in the field Experimental or Materials and Methods, Results and Discussion, Acknowledgments (when appropriate) and References.

Short Communications should be limited to 1500 words, including the equivalent space for figures and/or tables and should include an Abstract and concise Experimental.

Manuscripts may be submitted on-line or in triplicate (original and two copies by registered mail) and are received with the understanding that the original has not been submitted for publication elsewhere. It is implicit that all the persons listed as authors have given their approval for the submission of the paper and that permission has also been granted by the employer, when necessary.

Manuscripts must be written in American or British English, single spaced, on A4 sheets (21 cm x 29.5 cm) and one side only and should be numbered beginning with the title page. Type must be 12 Arial or Times New Roman.

Margins of at least 3 cm should be left at the top and bottom and both sides of each page. The first page of the paper should contain only the title of the paper, the name(s) and addressees) of the author(s), an abstract of not more than 250 words and 4-8 keywords. We reserve the right to translate the abstract in Portuguese. Abstracts are required of all papers including reviews and short communications.

Figures and Tables with short explanatory titles, each on a separate sheet, should be adequate for direct reproduction and identified in pencil on the back of each page by Arabic numerals, corresponding to the order they appear in the manuscript. Tables and Figures (BMP or JPG format) may also be included directly in the text when convenient and the article may submitted in a quasi-final form in order to facilitate editorial work.

References should be numbered in the sequence they appear in the text, cited by superior numbers and listed at the end of the paper in the reference section in the numerical order they appear in the text. The style for references is shown below:

1. L. G. Ionescu and D. S. Fung, *J. Chem. Soc. Faraday Trans. I*, *77*, 2907-2912 (1981).
2. K. L. Mittal, Ed., "*Solution Chemistry of Surfactants*", Plenum Press, New York (1984), Vols. 1-3, pp. 1-2173.

IUPAC Rules should be used for the name of chemical compounds and preference should be given to 51 units.

Authors are invited to send manuscripts by registered air mail to the EDITOR - SBJC, C.P. 15032, Agronomia, Porto Alegre, RS BRASIL 91501, or by e-mail to **lavinel@ibest.com.br** or **lavinel@pop.com.br**.

VISIT OUR SITE: http://www.sbjchem.he.com.br

SCIENCO
SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

ISSN 0104-5431

The *SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY - SCIENCO* publishes original research articles in chemistry and related interdisciplinary areas and is intended to fill a gap in terms of scientific information for Southern Brazil.

Occasionally the journal will include review papers and articles dealing with chemical education and philosophy and history of science. It will be published mainly in English, with abstracts in Portuguese and only occasional papers in other languages. At the present there are no page charges and the authors will receive twenty five reprints of their papers free of charge.

We have set high standards for the articles to be published by ensuring strong but fair refereeing by at least two reviewers. We hope that this journal will provide a forum for dissemination of high quality research in chemistry and related areas and are open to any questions and suggestions.

The Editor

SUBSCRIPTION INFORMATION

Brazil and Latin America:
US$ 35.00 per issue.

Other Countries: US$ 50.00 per issue, including air mail delivery. Persons or institutions outside Brazil should send subscription fee payable to Dr. L. G. Ionescu, c/o SBJC, 8532 Howard Circle, Huntington Beach, California, USA 92647

MAILING ADDRESS

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY - SBJC
Lavinel G. Ionescu, B.S., M.S., Ph.D., Editor
C.P. 15032, Agronomia
Porto Alegre, RS BRASIL 91501-000
Tel. (051) 485-1820 FAX (051) 339-1564

FINANCIAL SUPPORT

SARMISEGETUSA RESEARCH GROUP

SANTA FE, NEW MEXICO, U.S.A.

Endless Column, 1937, cast iron
CONSTANTIN BRANCUSI