



Volume 3, No 4, October 2011

ISAS newsletter is a quarterly email publication of Indian Society of Analytical Scientists composed and edited by Dr. V. Babu, Secretary - ISAS Kerala Chapter. He works as Scientific Officer in the R&D Department of Hindustan Insecticides Limited, Udyogamandal , 683501, Kerala State. To join the ISAS news letter mailing list, contact Dr V. Babu by e - mail babuv40@yahoo.co.in

Contents

Editors Notes	1
Message from President-ISAS	2
Indian Analytical Science Congress 2012	3
Abstracts of Contributed papers from ICAS 2010	10

Editor's Note:

Welcome to ISAS News Letter Volume 3, No 4. Readers may kindly send their comments /opinions/ suggestions, etc. to the editor by e-mail. I would like to thank all the contributors for the time and effort they have spent preparing the articles for this edition which I hope will be both informative and interesting.

Editor

MESSAGE FROM PRESIDENT-ISAS

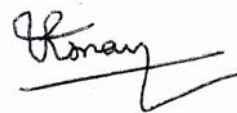
Dear Members,

As all of you are aware The International Congress on Analytical Science (ICAS 2010) organized at Cochin was a grand success with a strong forward looking technical programme embracing new techniques in analytical science. However, the distinctive feature of this event was the one day workshop on Molecular Probes which preceded the main conference. It has been decided to organize the next Indian Analytical Science Congress at Kanyakumari during January 2012. The theme of this congress is Analytical Chemistry for Energy, Environment and Life Sciences. There is national line-up of invited speakers from all over the country to address the most important of issues in the above areas .

During the last executive committee meeting it was decided to conduct the election to elect office bearers of the Executive committee. Election will be held during November-December 2012. A committee with Dr V. Babu as chairman has been constituted to conduct the elections. All members are requested to cooperate.

Once again I would like to inform all the members that we would like to maintain contacts with them . If there are any suggestions or comments you would like to make about what we are or are not doing please don't hesitate to get in touch with us (e-mail isaskerala@gmail.com).

I thank all the members for their continued support and hope to see you during IASC 2012 which will be held at Kanyakumari ,Tamil Nadu during January 2012. Once again I request all members to send us suggestions or comments they would like to make to improve the working of ISAS.



Indian Analytical Science Congress 2012

ISAS is organizing the next Indian Analytical Science Congress at Kanyakumari , Tamil Nadu during January 2012. The theme of the congress is, "Analytical Chemistry for Energy, Environment and Life Sciences".

SCOPE AND STRUCTURE

The aim of the proposed conference is to introduce young researchers to the present challenges for analytical science in the areas of Energy ,Environment and Life Sciences. Analytical chemistry assumes a prominent role in the field of energy, environment and life sciences. Energy use and supply are fundamentally important to society. With the possible exceptions of agriculture and forestry, the use of energy has had a greater impact on the environment than any other human activity-a result of the large scale and pervasive nature of energy-related activities. Although energy and environmental concerns were originally local in character-for example, health and safety issues associated with extraction, transport, or noxious emissions-they have now broadened in scope to cover regional and global issues, such as security, acid rain and the greenhouse effect. The economics of energy use and the cost of environmental control have become major political issues and the subject of extensive national and international debate and regulation . Environmental protection depends upon accurate sampling and chemical analysis of air, liquid and solid materials. Analytical tools have proven extremely useful for analysis of energy, environmental, and economic systems, facilitating credible, defensible decisions regarding large-scale deployment. Analytical chemistry contributes significantly to the life sciences through developing measurement techniques that provide quantitative chemical information. Developments in biological research present new challenges for analytical chemistry and call for revolutionary methods and new thinking. Analytical scientists play key roles in developing new technologies in the three areas . A variety of other topics will be presented and discussed in this conference by eminent speakers. Efforts will be made to identify the directions to which research in analytical chemistry have to move in order to respond to the problems faced by scientists working in the field of energy, environmental and life sciences. In this conference efforts will be made to cover the entire spectrum of analytical chemistry with special emphasis on topics related to energy,

environment and life sciences. The conference will focus on both traditional and emerging fields of analytical science. Professionals from various scientific fields are expected to attend the conference for deliberating and exchanging their current knowledge on scientific and technological issues related to applications of the analytical science and technology to decide on the future course of action. The conference also aims at networking scientists working in the area of analytical, energy, environmental and life sciences and those who are interested in knowing the new and latest developments in applications of analytical science . The conference is expected to provide excellent opportunities for both formal presentations and informal discussions for participants on various aspects of the applications of analytical science in the informal settings at Kanyakumari.

CONFERENCE DATE

January 27-28, 2012

LANGUAGE

The official language of the Conference is English

VENUE

The conference will be held at Hotel Singaar International, Kanyakumari

CLIMATE

The climate at Kanyakumari during January will be generally pleasant .The temperature will be between 20-25 degree Celsius.

PROGRAMME

The programme of the conference will consist of plenary/keynote/invited lectures by eminent scientists, contributed papers and posters by young scientists on a large variety of modern topics in analytical chemistry. Papers on the following topics on application of analytical science will be considered for oral or poster presentation at the conference :

Environmental analysis and measurements / Electroanalytical Methods.

- Analysis of food and Agricultural products·
- Analytical methods for the identification and determination of toxic compounds/metabolites.
- Application of Chemical and Biosensors .
- Application of Spectroscopic methods.
- Mining and mineral processing.
- Catalysts.
- Separation methods.
- X-Ray Techniques.
- Hyphenated techniques.
- Imaging Techniques.
- Trace Analysis and Speciation.
- Nuclear Industry.
- Thermal methods.
- Biotechnology .
- Forensic Analysis.
- Clinical and biochemical Analysis.
- Nuclear analytical methods.
- Pesticide analysis.
- Nanotechnology.
- Cosmetics analysis.
- Pigments analysis.
- Petroleum and Petrochemical analysis.
- Chemometrics and Statistics.
- Chromatography.
- Electrochemistry /Electrophoresis.
- Miniaturisation.
- Novel Assays.
- Sampling and sample handling.
- Spectrometry and spectroscopy .

In addition to these main categories, the scientific committee will accept contributions of papers that are relevant to the field of Instrumental Methods of Analysis in general, describing important new concepts, or providing insights of analytical processes and methods, as well as novel applications of analytical science in the area of energy, environment and life sciences. Contributions from commercial organizations are encouraged, including detailed descriptions of new

instrumentation, specific applications, and assessment of future commercial trends and opportunities.

EXHIBITION

An exhibition of analytical instruments, accessories, scientific books and journals will be held during the conference. Organizations interested in participating in the exhibition may contact the chairman, national organizing committee of the conference for details.

CALL FOR PAPERS

The organizing committee has great pleasure to request your participation in the conference and submit contributed papers dealing with any of the topics mentioned. An extended abstract of the technical paper should be submitted by e-mail to isaskerala@gmail.com or iascongress2012@gmail.com before 30 th, November, 2011. Authors will be notified of acceptance of abstract by December 15th, 2011.

REGISTRATION FEE

Participants of the conference are requested to register. The Registration Fee is set at Rs 4000/- if paid on or before 31 st, December 2011 and Rs 4500/- if paid afterwards. For ISAS Life members the registration fee will be Rs 2500/-. The fee entitles the participants to a conference kit, refreshments and lunch during the conference. Registration fee can be paid through crossed Demand Draft favoring IASC 2012 payable at Ernakulam and should reach the chairman - National organizing committee latest by 15th January 2012. Registration fee at site will be Rs 5,000/-. For students and research Scholars registration fee will be Rs 1500/-

AWARDS

There are awards for best contributed paper (oral and poster) presentation.

TRAVEL AND ACCOMMODATION

The participants are requested to make their own travel arrangements. Kanyakumari has a wide choice of good hotels with tariff ranging from Rs. 500 to Rs. 5000 /- per day. Accommodation may be arranged for outstation participants on request on payment basis in the hotels. Those desirous of availing the facility should clearly indicate the same in the accommodation form. They should send one day's rent in advance to

reserve their accommodation.

PATRONS

Dr Srikumar Banerjee, Chairman, Atomic Energy Commission
Dr Ramasamy, Secretary, Department of Science and Technology
Dr Samir Brahmachary, Director General-CSIR
Dr S.K.Jain, CMD ,NPCIL
Dr P.Suyambu , Chairman PSN Group of Institutions, Tirunelveli
Dr A.P. Majeed Khan, Chancellor, Noorul Islam University, Kumaracoil

NATIONAL ADVISORY COMMITTEE

Dr Suresh Das, NIIST, Thiruvananthapuram
Dr R.N. Patra, CMD, IREL, Mumbai
Dr. R. K. Bhandari, VECC, Kolkatta
Dr A. Ajayaghosh, NIIST, Thiruvananthapuram
Dr P.R. Vasudeva Rao, IGCAR, Kalpakkam
Dr. S. G. Markandeya, BRNS, Mumbai
Dr. K. Sreekrishna Kumar, Director, AICTE
Dr. P.P. Chandrachoodan, ATC, BRNS, Mumbai
Dr. G. N. Pandey, BRNS, Mumbai
Dr K.G.K. Warriar, NIIST, Thiruvananthapuram
Dr P.V.A. Padmanabhan, BARC, Mumbai
Shri A.K.Das, CGM-IREL, Udyogamandal
Dr M.L.P.Reddy, NIIST, Thiruvananthapuram
Dr D.Ramaiah, NIIST, Thiruvananthapuram
Dr Jose Panakkal, AFFF, Tarapur
Prof. R. Ramaraj, MKU, Madurai

NATIONAL ORGANIZING COMMITTEE

Dr. V.R. Nair, President- ISAS -Chairman
Dr. P. Unnikrishnan, Treasurer –ISAS-Convener
Dr. K.K.A.Rashid, Secretary- ISAS
Dr Raghaw Saran, Vice president-ISAS
Dr P.K.Jaiswal, Vice President-ISAS
Prof Srimannarayanan, Vice President-ISAS, Madras University
Shri Devraj Aiyer, SGE, Mumbai

Dr N.K. Pillai, Vice President-ISAS
Dr Anuradha Misra, Dupont Knowledge Centre, Hyderabad -78
Shri A.K. Mahapatra, IREL, Manavalakurichi
Dr S.C.Tripathi, BARC, Mumbai
Dr Daisy Joseph, NPD, BARC, Mumbai
Dr Vandita Srivastava, Praj Industries, Pune
Dr Jayasree, SCTIMST, Thiruvananthapuram
Dr V Natrajan, BARC, Mumbai

LOCAL ORGANIZING COMMITTEE

Dr P.N.Mohandas – Chairman Former Deputy Director, NIIST Trivandrum
Dr A.Sundaresan - Convenor, NIIST, Trivandrum
Prof. A.G. Murugesan, SPKCESS, MSU, Alwarkurichi
Dr J.K.Patterson, SDMRI, Toothukudi
Dr Gopinathan Nair, Travancore Titanium Products, Trivandrum
Dr. M.P. Rajan, KKNPP, Kudankulam
Shri S.S.Kumar, DGM, IREL, Manavalakurichi
Dr Shahaya Shajan, PSNCET, Tirunelveli
Shri P.K.Jena, DGM, IREL, Manavalakurichi
Dr S.Godwin Wesley, Scott Christian College, Nagecoil
Dr P.Narayanan, IREL, Udyogamandal
Dr V.Babu, HIL, Udyogamandal
Shri S.Arun Kumar, IREL, Mumbai
Dr Balakumar, PSNCET, Tirunelveli

Address or correspondence:

Chairman - National Organizing Committee

Dr V.R.Nair-President-ISAS

Geethanjali,
Puthalathu Kadavu Road
Near X Pius Church, N.Kalamasserry
683104, Kerala state
Phone 0484-2556366
mobile +91-9447369769

Convener National Organizing Committee

Dr P.Unnikrishnan-Treasurer-ISAS,

Sr. Manager(QA)- Sud Chemie India(P)Limited,
Edayar Industrial area, Binanipuram-683502
Aluva, Kerala State

Phone 0484- 6646026
mobile : +91 9447769916

e-mail isaskerala@gmail.com / iascongress2012@yahoo.co.in

Chairman-Local Organizing Committee

Dr P.N.Mohandas-Former Dy.Director,
NIIST, CSIR, Trivandrum.
Indeevaram SKNRA 22A, Sreekrishna Nagar,
Jagathy, Thiruvananthapuram 695 014
Phone 04712115005 mobile+91- 9847410720
e-mail daspnm@rediffmail.com

Convener-Local Organizing Committee

Dr A.Sundaresan-Scientist,
National Institute for Interdisciplinary Science and
Technology, CSIR,Industrial Estate P.O.,
Thiruvananthapuram -695 019
Phone:0471-2515-234 mobile +91-9249577828
e-mai : a_sundaresan@niist.res.in

CONTRIBUTED PAPERS FROM ICAS 2010

(ICP-1 to 40 were published in the previous newsletter)

ICP-41

A GOLD NANO PARTICLE-CYSTEINE-METAL HEXACYANOFERRATE (II) GRAPHITE COMPOSITE ELECTRODE FOR THE DETERMINATION OF BHA

G. Sivasankari and S. Sriman Narayanan*

Department of Analytical chemistry, University of Madras

Abstract

The use of antioxidants in the food and pharmaceutical industries is particularly important to prevent the decomposition of organic compounds present in prepared products. Biological and toxicological aspects, detection, estimation and evaluation of antioxidants used as food additives have been described by Hudson[1]. BHA is one of the most commonly employed antioxidant. While cooking or baking at higher temperatures it remains active without undergoing decomposition. So it is exclusively used in food products. Different type of voltammetric procedures have been reported for the determination of BHA. In the development of chemically modified electrodes (CMEs) there as been considerable interest in recent years, as they offer a lot of advantages over other electrochemical methods. CMEs improve the sensitivity and selectivity of electrochemical analysis by improving the kinetics of the reaction via an electrocatalytic process at the CME surface. A Nickel hexacyanoferrate(II)-L-cysteine-gold nano particle (NiHCF-L-Cys-GNP) graphite wax composite electrode was prepared for determination of butylated hydroxyanisole (BHA) which is being used as antioxidant in processed foods. This electrode has favorable properties with respect low cost, simple preparation and easy renewal of the electrode surface. GNP present in the electrode display four unique advantages over macro electrodes when used for electro analysis: enhancement of mass transport, catalysis, high surface area and control over electrode microenvironment [2].

The modified electrode was characterized by SEM, FTIR, different electrolytes, scan rates and pH. The modified electrode showed good electrocatalytic activity towards the oxidation of BHA (Fig.1) under the optimal conditions and showed a linear response over the range from 4.9×10^{-6} to 1.03×10^{-3} M of BHA with a correlation coefficient of 0.999. The limit of detection was found to be 1.2×10^{-6} M. The analytical utility of the electrode for determination of BHA in flow system was evaluated by hydrodynamic and chronoamperometric studies. Differential pulse voltammetry (DPV) and flow injection techniques were also used for the determination of the analyte from commercially available biscuits samples spiked with BHA.

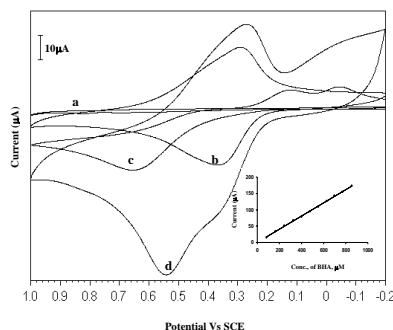


Fig.1.Cyclic voltammograms in 0.1 M NaNO₃ (pH 7.0) at a scan rate of 20 mVs⁻¹ (a, b) bare and modified electrode in the absence of BHA (c, d) bare and modified composite electrode in the presence of 7.6x10⁻⁵M BHA. The inset shows the calibration graph for BHA determination.

Keywords:

GNP; Nickel hexacyanoferrate; Electro catalysis; BHA.

Reference:

1. B.J.F Hudson, Journal of Food antioxidants, London: Elsevier. (1990) (pp.5-7).
2. B K Pong, I Hendry Elim, J X Chong, W Ji, L Bernhart Tront and J Y Lee,
Journal of Phys. Chem. C **111**, (2007) (6281-6287).

ICP-42

ELECTROCATALYTIC BEHAVIOR OF L-DOPA BASED ON IONIC LIQUID-NICKEL HEXACYANOFERRATE NANOPARTICLE MODIFIED ELECTRODE

R. Suresh Babu and S. Sriman Narayanan*

Department of Analytical Chemistry, School of Chemical Sciences, University of Madras, Guindy Campus,
Chennai- 600 025, Tamil Nadu, India

*E-mail: sriman55@yahoo.com

Abstract

Levodopa (L-dopa), beta-(3, 4-dihydroxyphenyl)-L-alanine, the medication of choice for the treatment of Parkinson's disease, is principally metabolized by an enzymatic reaction (dopa decarboxylase) to dopamine compensating for the deficiency of dopamine in the brain [1]. Once transported to the brain, it is converted into dopamine and stored in nerve cells to replace the depleted dopamine. Chronic L-dopa treatment in Parkinson's disease patients is frequently associated with some side effects such as nausea and vomiting results from the increases of plasma L-dopa level. Thus, it is very important to have an analytical technique for the determination of L-dopa in biological fluids and pharmaceutical preparations.

Electrochemical methods offer useful alternatives since such analysis is faster, cheaper and safer. However, the oxidation of L-dopa at bare electrode involves a large overpotential. One of the most promising methods is to modify the electrode surface with suitable catalyst, which not only improves the oxidation of L-dopa, but also provides a means of extending the dynamic range in analytical determinations.

Metal hexacyanoferrate (MHCF) modified electrodes have been investigated intensively for a variety of applications including electrocatalysis, ion-selectivity, electrochromism and solid state batteries. In this study, NiHCF nanoparticle modified electrode is used as an electron-transfer mediator for developing amperometric sensors.

Recently, room temperature ionic liquids (RTILs) have been proposed to be very interesting and efficient binders instead of non-conductive organic binders for the preparation of carbon composite electrodes due to their high viscosity [2]. RTILs are liquids composed entirely of ions and exist in the liquid state near room temperature. They have several characteristic properties, including intrinsic conductivity, low (or near zero) volatility, high polarity, good chemical and thermal stability, almost negligible vapor pressure, low toxicity and wide electrochemical windows. They are increasingly being used in applications such as green synthesis [3], catalysis with transition metals, and in electrochemical applications such as electrodeposition of metals [4], as electrolytes in lithium batteries, capacitors, fuel cells and in electrochemical sensors [2].

In the present work, the modified electrode was constructed using nickel hexacyanoferrate nanoparticle mixed with 1-ethyl-3-methylimidazolium tetrafluoroborate as a binder instead of other non-conducting pasting binder. The NiHCF-NP-RTIL-gel composite was immobilized on the surface of the paraffin wax impregnated graphite electrode, which was used as L-Dopa sensor. The modified electrode was characterized by cyclic voltammetry and electrochemical impedance spectroscopy and scanning electron microscopy. Electrocatalytic oxidation of L-Dopa was performed using cyclic voltammetry and amperometric method is proposed for the determination of L-Dopa. The sensor exhibits good stability and reproducibility.

Keywords: Nickel hexacyanoferrate nanoparticle, Room temperature ionic liquid, L-Dopa

References

- [1] W.J. Weiner, Parkinson's disease: Diagnosis & Clinical Management, Demos Medical Publishing, New Work, 2002, 195.
- [2] D. Wei, A. Ivaska, *Anal.Chim.Acta*, 607, 2008 126
- [3] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39, 2000, 3772.
- [4] F. Endres, *ChemPhysChem*, 3, 2002, 144.

ICP-43

ELECTROANALYSIS OF VANILLIN BY CuHCF SURFACE MODIFIED GOLD NANOPARTICLE GRAPHITE COMPOSITE ELECTRODE

P. Prabhu and S. Sriman Narayanan*

Department of Analytical Chemistry,

School of Chemical Sciences,

University of Madras,

Guindy Campus, Chennai- 600 025

Tamil Nadu, India

e-mail: sriman55@yahoo.com

Abstract

Vanillin (4-hydroxy 3 –methoxy benzaldehyde), the major constituent of vanilla beans, is one of the most important aromatic flavor compounds used in foods, beverages, perfumes and pharmaceuticals in large scale. Vanillic acid and protocatechuic acid are the catabolic products obtained along with vanillin from ferilic acid degradation. Like many polyphenols found in plants, vanillin also exhibits antioxidant, anti-tumour, anti-mutagenic activity and also inhibits chemical carcinogenesis. Vanillin was oxidized investigated by copper hexacyanoferrate (CuHCF) film modified cysteamine gold nanoparticle (AuNp) graphite paraffin wax composite electrode (GWCE). The electrode was constructed by a new fabrication method. Self assembled monolayers (SAM) using organo-sulfur compounds to develop prussian blue (PB) analogues modified electrodes has attracted researchers to develop a tailored mono or multilayer on the bare electrode to either electrodeposit or to anchor dyes and redox mediators to improve the sensitivity and selectively of detection. Recently few papers have been reported on SAM of metal hexacyanoferrate (MHCF) using organo thiol compounds (cysteamine) on gold nanoparticle deposited either on gold electrode or glassy carbon electrode [1-2]. Cysteamine (2-aminoethanethiol) is a short chain organic linker with a thiol (-SH) terminal at one end which holds the gold nanoparticle and an amino (-NH₂) at the other terminal, which has a good affinity to transition metal ions like Ni²⁺, Co²⁺, Cu²⁺ etc., and helps to develop stable and insoluble inorganic ferrocyanide film on the electrode surface. In the current work, we have fabricated a copper hexacyanoferrate (CuHCF) film modified gold nanoparticle (AuNp) – cysteamine - capped graphite composite electrode with the help of paraffin wax as a binding matrix. The modified composite electrode exhibited a well resolved pair of redox peaks at 685 mV anodic and 624.5 mV cathodic with a formal potential of 654.75 mV, corresponding to the anodic and cathodic reactions respectively in 0.1 M KCl at the scan rate of 20mVs⁻¹. Electrochemical impedance spectroscopy (EIS) parameters such as R_{ct}, C_{dl}, R_s and Z_w were found to be 28.35 kΩ cm⁻², 12.29 nF cm⁻², 303.6 kΩ cm⁻² and 8.778 x 10⁻⁴ Ω cm⁻²s^{1/2} respectively. The charge transfer resistance (R_{ct}) to the electron transfer kinetics of the CuHCF film on the cysteamine Au-colloid composite electrode was comparatively close to the bare electrode. The influence of ultrasonication on stability and diffusion phenomenon of modified electrode was also studied. The range of detection was found to be 6.2 x 10⁻⁶ M to 1.2 x 10⁻⁴ M and the limit of detection is found to be 1.5 x 10⁻⁶ M with a good sensitivity. Real time

analysis of vanillin in commercially available coco powder with the modified electrode was also investigated and the results were quite satisfactory.

Keywords: *Gold nanoparticle; cysteamine; copper hexacyanoferrate; vanillin.*

References:

1. W. Tao, D. Pan, Y. Liu, L. Nie, S.Yao J. Electroanalytical Chemistry 572 (2004) 109–117.
2. J. A. Lopez, J. Manriquez, S. Mendoza, L.A Godionez, Electrochemistry Communications 9 (2007) 2133–2139.

ICP-44

ELECTROCHEMICAL BEHAVIOUR OF AZURE A FUNCTIONALIZED GRAPHITE MODIFIED ELECTRODE TOWARDS THE SIMULTANEOUS DETERMINATION OF DIHYDROXYBENZENES

C. Priya and S. Sriman Narayanan*

Department of Analytical chemistry,

School of Chemical Sciences, University of Madras

Guindy Campus, Chennai – 600 025

Tamil Nadu, India

e-mail: sriman55@yahoo.com

Abstract

The phenothiazine dyes are very attractive because they are chemically reactive and exhibit negative formal potential at neutral pH [1, 2]. Several carbon materials are widely used in electrochemistry for the fabrication of modified electrodes [3, 4]. Among these, the graphite powder was mostly preferred due to its low cost, high electrical conductivity and suitable thermal stability. An electrochemical sensor was developed based on the immobilization of Azure A (one of the phenothiazine derivative dye) with oxidized graphite powder (OGP) through carbodiimide coupling method. The Azure A functionalized graphite powder was characterized by spectroscopic and electrochemical methods. The development of an electrochemical sensor was achieved by casting the dispersed methanolic solution of AA functionalized graphite powder on the paraffin impregnated graphite electrode (PIGE). A 0.5% Nafion (Nf) solution was dropcasted on the surface for improving the

stability of the electrode. The modified electrode shows a distinct redox peaks with an anodic potential of - 0.078V and a cathodic potential of -0.2492V in 0.1M PBS (pH 7). The formal potential E_f^0 was found to be -0.15 Vs SCE. The effect of scan rate and the effect of pH have also been studied.

The studies showed that the prepared electrode exhibits excellent electrocatalytic behaviour for the oxidation of dihydroxybenzene isomers. The o-, m- and p-dihydroxybenzene isomers are important environmental pollutants and they are difficult to degrade. Due to their similar structures and properties, they usually coexist and interfere with each other during their determination. Therefore it is very important to develop simple and rapid analytical methods for the determination of dihydroxybenzene isomers (Hydroquinone (HQ) Catechol (CC) and Resorcinol (RE)).The immobilization of AA with graphite powder facilitates mediated electro oxidation of dihydroxybenzenes. The modified electrode shows an oxidation peak at 0.052V, 0.170V and 0.552V for HQ, CC and RE respectively. This modified electrode can also be used as an amperometric sensor for the determination of dihydroxybenzenes. Moreover, the modified electrode greatly reduced the oxidation over potential and has a great advantage of low cost, easy fabrication, reproducibility and stability. The electrode developed can also be used for the analysis of some other biological compounds.

Keywords: Azure A, oxidized graphite powder, carbodiimide, dihydroxybenzenes,

References

- 1) M. Arvind, S. Sohrabnezhad, M.F. Mousavi, M. Shamsipur, Ma. Zanzanji, Anal. Chim.Acta. 491 (2003) 193-201.
- 2) S.A. John, R.J. Ramaraj, Electroanal. Chem. 76 (2004) 474-8
- 3) A.J. Downward, Electroanalysis. 12 (2000) 1085-96
- 4) L. Rabinovich, O. Lev, Electroanalysis. 13 (2001) 265-75

ICP-45

PREPARATION, CHARACTERIZATION AND ELECTROCHEMICAL PROPERTIES OF MnO₂/MONT K10 NANOCOMPOSITE

B. Vijayakumar*, P. Justin and G. Ranga Rao*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036.

* Corresponding Author: Phone No +91-44-22575230, badathala@rediffmail.com (B. Vijayakumar),
Phone No +91-44-22574226, grrao@iitm.ac.in (G. Ranga Rao)

Abstract

Nanostructured materials have unique physical and chemical properties and wide applicability as catalysts and sensors and in energy storage (lithium secondary battery, solar cell, supercapacitor, and fuel cell) [1-4]. Particularly, there has been intense research on energy storage to satisfy the present day demand for high and continuous power supply to drive the fast-changing development in wireless communication equipments and electric transportation [5]. Among the energy storages devices, electrochemical supercapacitors have gained special interest [6,7].

In this paper, MnO₂/mont K10 nanocomposite has been prepared by reacting KMnO₄ and ethylene glycol in presence of montmorillonite K10 at room temperature. The nanocomposite has been characterized by X-ray diffraction, BET specific surface area (154 m²/g) and pore size analysis (mesopores of diameter 3.4 and 5.5 nm), infrared spectroscopy, UV-Vis diffuse reflectance spectroscopy, thermogravimetric analysis, and scanning electron microscopy for its physicochemical properties. The electrochemical studies have been carried out in a three electrode-configuration-cell with Ni foil coated with MnO₂/mont K10 as working electrode, platinum foil as counter electrode and Hg/HgO (1.0 M KOH) as reference electrode, all dipped in 0.5 M Na₂SO₄ aqueous electrolyte. The MnO₂/mont K10 nanocomposite showed remarkable specific capacitance of about 255 F g⁻¹ over 100 cycles at a current density of 500 mA g⁻¹ in a life cycle test.

Keywords: MnO₂/mont K10, montmorillonite K10, nanocomposite, electrode, supercapacitor.

References

- [1] H.-S. Qian, M. Antonietti, S.-H. Yu, *Adv. Funct. Mater.*, **17**, 637 (2007).
- [2] S. Shanmugam, A. Gedanken, *Small*, **3**, 1189 (2007).
- [3] P. W. Barone, M. S. Strano, *Angew. Chem., Int. Ed.* **45**, 8138 (2006).
- [4] H. Zhang, Q. Zhu, Y. Zhang, Y. Wang, L. Zhao, B. Yu, *Adv. Funct. Mater.*, **17**, 2766 (2007).
- [5] B. E. Conway, *Electrochemical Supercapacitors, Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum, New York, (1999).
- [6] P. Ragupathy, D.H. Park, G. Campet, H.N. Vasan, S.-J. Hwang, J.-H. Choy, N. Munichandraiah, *J. Phys. Chem. C*, **113**, 6303 (2009).
- [7] P. Justin, S.K. Meher, G. Ranga Rao, *J. Phys. Chem. C*, **114**, 5203 (2010).

ICP-46

REMEDIATION OF PHORATE CONTAMINATED SOIL USING IRON NANO-PARTICLES

*B. Gangadhar ^a, R. K. Singhal ^b, Y. Tharakeswar ^a, Manisha Venkatesh ^b, H. Basu ^b, G.R.K. Naidu ^a and A.V. R. Reddy ^b

^a Department of Environmental Sciences, S.V.University, Tirupati, Andhra Pradesh, India

^bAnalytical Chemistry Division, Bhabha Atomic Research Centre, Mod-Labs, Trombay, Mumbai - 400 085, India

Abstract

In the present study Iron nano-particles were prepared and used to remediate phorate contaminated soil in the concentration range of 1 – 10 ppm. Phorate (O,O-diethyl S-ethylthiomethyl phosphorodithioate) is an organophosphorus insecticide and acaricide used to control sucking and chewing insects, leaf hoppers, leaf miners, mites, some nematodes, and root worms . Phorate is used in pine forests and on root and field crops, including corn, cotton, coffee, some ornamental and herbaceous plants, and bulbs. Phorate is of moderate persistence in the soil environment, with reported field half-lives of 2 to 173 days. The nano-particles of iron were prepared by reducing ferric chloride solution ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) using, sodium borohydride (NaBH_4). 1.6 M sodium borohydride was added drop-wise into 0.2 M of ferric chloride solution to produce iron nano-particles. The high concentration difference between the two solutions leads to the formation of iron nano-particles. Hydrodynamic diameter of the particles was measured by using zeta sizer based on Dynamic Light Scattering (DLS). The synthesized iron nano particles were able to remediate the Phorate contaminated soil. It was found that the amount of destruction decreases as the amount of nano-particles is decreased from 1 g to 0.1g for every 10 g of soil. However, the decrease in Phorate destruction was not proportional to the decrease in the amount of nano-particles. To make the process economical, 0.1 g of nano-particles were used for every 10 g in all remaining experiments.

* Corresponding author Ph. 91-9347894951, E-mail: gangadhar.battala@gmail.com

ICP-47

A GEL PERMEATION CHROMATOGRAPHY (GPC)METHOD FOR SIMULTANEOUS DETERMINATION OF 1,4-BUTANEDIOL (BD) AND 1,1,1-TRIMETHYLOPROPANE(TMP) IN THE MIXTURE

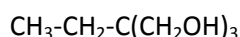
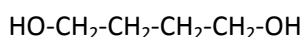
¹Vijendra Kumar, ¹S.Chandrakumari Amma, ²S.K. Manu, ¹G. G. Bandyopadhyay

¹Analytical Division, ²Propellant Fuel Complex, Chemical Systems Group,
Propellants, Polymers, Chemicals and Materials, Vikram Sarabhai Space Centre,
Indian Space Research Organization, Thiruvananthapuram – 695022

Email: vkvssc@gmail.com, vijendra_kumar@vssc.gov.in

Abstract

A new analytical method based on Gel Permeation Chromatography (GPC) is developed for simultaneous determination of 1,1,1-trimethylolpropane (TMP) and 1,4-butanediol (BD) in the mixture by measuring the corresponding GPC peak area. Both BD and TMP are primary alcohols having the following formula:

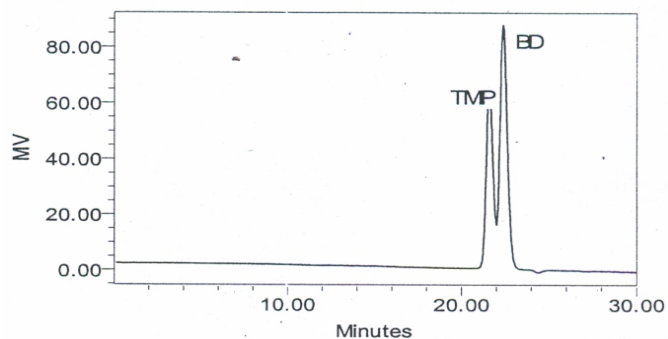


BD (1,4-Butanediol), MW: 90.12

TMP (1,1,1-Trimethylolpropane), MW: 134.18

In the cross-linked network of propellant formulation, BD acts as chain extender while TMP functions as cross-linker, therefore any deviation from the optimal ratio of BD and TMP will result poor propellant mechanical properties. Determination of TMP and BD in a mixture by GPC method is based on difference in their molecular weights (hydrodynamic volume) in the solution. Small molecules (less than 2000 MW) can generally be separated if their size in solution differs by approximately 10%. The samples were analysed using a GPC system comprising of Waters[®] 515 HPLC pump, Rheodyne 7725i injector, and Waters[®] 410 Differential Refractometer [1]. Separations were performed using two Waters[®] μ Styragel 7.8mm x 300mm (500A[°] and 100A[°], 15 μ) columns (stationary phase) and an eluent (Tetrahydrofuran-THF, mobile phase) having flow rate of 0.8 ml/min [1]. The columns and detector were thermostated at 30[°]C. Samples were prepared at 1.0% w/w in Tetrahydrofuran (THF) and allowed to dissolve at ambient temperature and the injection volume was 150 μ l. Best possible separation between the two peaks obtained at the above-defined instrumental conditions with acceptable chromatographic resolution of 0.9825. The GPC data acquired and analyzed using Empower 2 software.

Individual linear calibration curves established by taking various concentrations (from ~0.2% to 1.4% w/w in THF) of TMP and BD and their corresponding detector response (Area, $\mu\text{V} \times \text{sec}$) respectively. Correlation coefficients for TMP and BD obtained from GPC



**Fig. Typical GPC chromatogram for
TMP and BD analysis**

(r value 0.99979 for TMP and 0.99968 for BD) show excellent linear correlation between dependent (detector response) and independent (sample concentration) variables. Regression analysis performed by analyzing peak area data of TMP and BD and correlating with linear calibration plots of TMP and BD to obtain corresponding concentrations of TMP and BD in the mixture. Following table summarizes the correlation between instrumental response and actual amount of custom-made samples.

Table: Comparison of Actual value with the GPC value for different TMP and BD

concentrations.

Sl. No.	Actual Value (Ratio of TMP and BD)		GPC value (Ratio of TMP and BD)	
	TMP (%)	BD (%)	TMP (%)	BD (%)
1.	19.25	80.75	18.04	81.96
2.	30.01	69.99	28.56	71.44
3.	40.99	59.01	39.66	60.34
4.	48.75	51.25	47.49	52.51
5.	58.90	41.10	57.91	42.09

6.	77.64	22.36	77.67	22.33
----	-------	-------	-------	-------

Reasonable correlation observed between the instrumental response and actual amount of TMP and BD. Based on the calibration data of TMP and BD, the relative concentration of TMP and BD in the mixture can be determined simultaneously.

References

1. Elizabeth Meehan, "Characterisation of hydroxypropylmethylcellulose phthalate (HPMCP) by GPC using a modified organic solvent", *Analytica Chimica Acta* 557 (2006) 2-6.
2. Sonia Morante-Zarcero, Isabel del Hierro, Mariano Fajardo, Isabel Sierra, "Development and validation of a chiral HPLC method for rapid screening of allylic alcohol asymmetric epoxidation processes", *Analytica chimica acta* 618 (2008) 102–109.

ICP-48

PRECONCENTRATION OF TRACE METALS IN ENVIRONMENTAL SAMPLES BY AMBERLITE XAD-16 COATED WITH TRIAZOLE AND DETERMINATION BY ICP-AES

B. Naresh Kumar, N. Seshadri, D.K.V. Ramana and K.Seshaiah *

Analytical and Environmental Chemistry Division, Department of Chemistry,

Sri Venkateswara University, Tirupati, Andhra Pradesh, India

E-mail: seshaiahsvu@gmail.com

Abstract

A new ligand, 3-(3-nitrophenyl)-1H-1,2,4-triazole-5(4H)-thione (NPTT) was synthesized and used for the functionalization of amberlite XAD-16 resin. Amberlite XAD-NPTT was characterized by IR, NMR spectral studies. Application of the functionalized resin for the solid phase extraction (SPE) of Ni(II), Cu(II), Cd(II) and Zn from water prior to their determination by Inductively coupled plasma atomic emission spectrometry (ICP-AES) was investigated.. Several parameters like the effect of pH, effect of sample volume and flow rate, concentration of eluent, sorption capacity and the effect of diverse ions on the

sorption of analytes were investigated. All the metal ions were quantitatively retained by the functionalized resin at pH 5.0 and sorbed metals were eluted with 1.5 M HNO₃. The detection limits were 0.4, 0.4, 0.1, 0.5 µg L⁻¹ for nickel, copper, cadmium and zinc respectively. The method was applied for the determination of trace metal ions in sea water and natural water samples.

ICP-49

ESTIMATION OF POTASSIUM NITRATE IN PYROTECHNIC COMPOSITIONS BY NON AQUEOUS POTENTIOMETRIC TITRATION

K. S. Abhilash, Bismi Basheer and Benny K. George

Analytical and Spectroscopy Division

Vikram Sarabhai Space Centre, Trivandrum 695055

ks_abhilash@vssc.gov.in

Abstract

Pyrotechnic charges are extensively used in various aerospace systems and devices like squib, cartridge, igniter, booster, delay charge, cable cutter and valve to carry out a number of critical mission functions. A typical pyrotechnic system consists of inorganic oxidizers like potassium nitrate or chlorate, a metal powder like boron or zirconium and additives like lead thiocyanate, lead ferro cyanide, calcium silicide etc.

Estimation of potassium nitrate (KNO₃) in various pyrotechnic compositions is a critical parameter in the quality check of the composition before its actual use. There are different methods available in literature for the estimation of assay of KNO₃ like Luge-Sedehol's method using nitrometer ^[1] and Devarda's Alloy method ^[2] followed by Kjeldahl's method. These methods are tedious and less accurate unless all precautions are followed. Conventionally, the estimation is being done using ion exchange column ^[3]. Eventhough the method by ion exchange column is simple, it is very slow and is prone to several types of inaccuracies. Non-aqueous potentiometric titration is a suitable method in many situations where solubility of analyte in water is less or use of visual indicators is not applicable.

Here, we report a method especially suited for the routine analysis of KNO₃ in pyrotechnic compositions. Potentiometric estimation of potassium nitrate in AR KNO₃ and in two pyro compositions viz., i) Boron - KNO₃ ii) Zirconium - KNO₃ using different non aqueous solvents ^[4, 5] and titrants were attempted. Acetic acid, chloroform, acetonitrile, p-dioxane etc were used as solvents and perchloric acid/chloroform, perchloric acid / acetic acid etc as titrants. These analyses were carried out using a Mettler Toledo autotitrator, Model DL55 with combined glass electrode DG-113 SC. The method was cross-checked by

ion exchange column method. Synthetic samples of pyrocharges, prepared by mixing KNO_3 with known quantities of boron or zirconium, were used for method validation. The results are shown in the following table.

Sample	KNO_3 (%)		
	Theoretical	Ion exchange method	Non aqueous potentiometry
KNO_3 (AR)	99.0	99.3	99.1
Boron - KNO_3	75.0	75.2	74.9
Zirconium - KNO_3	50.0	50.3	50.1

The non-aqueous potentiometric method developed for the estimation of KNO_3 is simple, fast and moreover safe to be adapted for the routine in-process quality check of pyrotechnic compositions. This method is superior in the sense that it is less time consuming and does not require any complex analytical methodology or experimental setup.

References

1. A B Bofors, Nobelkrut, Analytical methods for powders and explosives, Bofors, Sweden, 1960, pp. 104.
2. Christina. F. H. Liao. Soil Sci Soc Am J, **45.**, 852-855 (1981)
3. Harold. F. Walton, Analytical applications of ion exchangers, Pergamon press, Oxford, 1966
4. Sarson. R. D. Anal. Chem., **30 (5).**, 932-937 (1958)
5. Gary Wulfsberg, Inorganic chemistry, University science books, CA, 2000, 175-180

ICP-50

A NEW FUNCTIONALIZED RESIN FOR SOLID PHASE EXTRACTION OF URANIUM(VI) FROM ENVIRONMENTAL SAMPLES

D. Harikishore Kumar Reddy^a, Y. Harinath^a, K. Sessaiah^{a*}, A.V.R. Reddy^b

^a Department of Chemistry, Sri Venkateswra University, Tirupati, India.

^b Analytical Chemistry Division, Bhabha Atomic Research Center, Trombay, Mumbai, India.

Abstract

A simple and sensitive column solid-phase extraction procedure for separation and preconcentration of U(VI) from natural water samples using Terephthalaldehyde bis(thiosemicarbazone)-functionalized Amberlite XAD-16 (XAD-16-TBT) resin prior to the determination by inductively coupled plasma atomic emission spectrometry has been developed. The new chelating resin was prepared by coupling terephthalaldehyde bis(thiosemicarbazone) to Amberlite XAD-16 through an azo spacer. The functionalized resin was characterized by elemental analyses, FTIR, SEM, XRD and TG-DTG. The optimum experimental parameters such as pH (6.0), volume of sample (~250 mL), flow rate of the sample (2.5 mL min⁻¹), and volume of the eluent (2 mol L⁻¹ HNO₃, 20 mL) and sorption capacity of the chelating resin, were evaluated. The effect of the electrolytes and the cations on the preconcentration of metal ion was also investigated. The chelating resin could be reused for more than 10 cycles of sorption–desorption without any significant change in the sorption capacity. Studies with spiked samples for the optimization of the method showed that a recovery of >92 % of the analyte was achieved with the developed resin. The present method has been successfully applied to the determination of the U(VI) in natural water samples collected from Kadapa district (Andhar Pradesh, India) water samples with good results such as relative standard deviation.

ICP-51

CIRCULAR DICHROSIM STUDIES OF THE BINARY COMPLEX FORMATION BETWEEN GLYCOSYLATED HAEMOGLOBIN And 4-VINYLPHENYL BORONIC ACID

Jingal Vasani^{*}, Rahul George Mathew, Aparna Sil, Koteppa Pari, Venkat Manohar

Department of Analytical Sciences

Piramal Life Sciences Ltd.

Abstract

Owing to the severe and increasing occurrences of Type-1 and Type-2 diabetes in the recent years, management of these metabolic syndrome related diseases are a major concern. Monitoring the levels of blood glucose and glycated haemoglobin (HbA1c) has been used in the management of diabetes related disorders. It is already known that the level of HbA1c is directly correlated to the amount of glucose in the blood and hence among other approaches that exist, to monitor the blood glucose level in patients, monitoring the levels of glycated haemoglobin is being used extensively as one of the best approaches. The developments of saccharide linked boronic acid sensors to monitor the glycated hemoglobin levels have gained tremendous attention since the past few years [1]. It has been reported that boronic acid and cis-diols are known to form the strongest signal pair reversible functional group interaction in an aqueous environment. Accordingly, sugars with 1, 2-diol groups have been observed to react intramolecularly with boronic acid moieties, thereby rendering optical activity to the complex thus formed. Complexation of such kind has been monitored employing different spectroscopic techniques (viz, fluorescence techniques) [2]. Reports also exist on the use of ***Circular dichroism (CD) as a tool for monitoring the complex formation between different class of diols and boronic acid*** [2]. ***CD being a sensitive spectroscopic technique*** is commonly used to investigate the structure and conformations of proteins, nucleic acids and other chiral biomolecules [3]. In the present study, CD has been utilized as a tool to detect the binding of 4-VinylPhenyl Boronic acid (VPBA) to the glycosylated hemoglobin (HbA1c). The CD spectra obtained for the physical mixture of 1:1 D-glucose and VPBA (in comparison to a standard CD maximum at 300 nm observed for D-glucose), clearly indicated a low affinity binding between the free D-glucose and VPBA. Similar observations have been reported for the same complex recently [4]. However, in the subsequent CD studies that were carried out, the same VPBA exhibited a strong binding affinity towards glycated haemoglobin, corroborating the existence of a strong binary complex between VPBA and the HbA1c. The mechanism through which this strong complexation occurs is not clear yet, but it is assumed that a symmetrical change in the boronic acid that affords it a tetrahedral nature. And the tetrahedral boronic acid in turn is believed to have a strong propensity to form a binary complex with the HbA1c bound sugar. A strong CD curve with a maximum at 420 nm observed for the binary mixture containing VPBA and HbA1c has been attributed to the (sugar) signal arising as a result of strong complex formation between the sugar and the boronic acid. However it is not yet clear how many boronic acid moieties bind to a sugar residue in the glycated haemoglobin, but based on the earlier studies that have been reported in the literature [2], it is assumed that two boronic acid moieties per sugar residue of the HbA1c are involved in the complex formation. Results obtained from the current studies find their importance in the fact that, CD technique can be used as a tool to obtain precise and clear information on the possible symmetrical and conformational change that occurs upon complex formation between sugars and boronic acids. Symmetrical change that occurs with boronic acid has a major role to play in the design of molecular sensors involving these molecules.

Reference:

1. H.B. Chandalia and P.R. Krishnaswamy, *Current Science*, 83, 1522-1532, (2002).
2. M. Takeuchi, T. Imada and S. Shinkai, *Bull.Chem.Soc.Jpn.*, 71, 1117-1123, (1998).
3. A. Parra and E.S. Stevens, *Carbohydrate Polymers*, 41, 111-113 (2000).
4. N. Kanayama and H. Kitano, *Langmuir*, 16, 577–583 (2000).

* Corresponding Author

E-mail: jingal_v@yahoo.co.in, nmr.spectroscopy@pir

ICP-52

SPECTROPHOTOMETRIC DETERMINATION OF SILICON AND IRON IN MAGNESIUM METAL

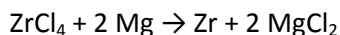
K. Madhava Krishna, Vijaya Rammohan and R.B. Yadav

Control Laboratory, Nuclear Fuel Complex, ECIL (PO), Hyderabad 500062, A.P. India

Email: rby@nfc.gov.in

Abstract

A simple spectrophotometric method is described for the determination of trace quantities of silicon and iron in magnesium metal that is used in the Kroll's reduction process for the production of nuclear grade zirconium sponge. In Kroll's process, zirconium sponge is produced by the magnesium - thermic reduction of pure $ZrCl_4$ by pyrovacuum treatment of the reduced mass to separate excess Mg and $MgCl_2$ from Zirconium. The magnesium - thermic reduction involves the following reactions.



The production of nuclear grade Zirconium sponge demands close control of quality of raw material and process parameters at various stages. Hence it is important to confirm the purity of Mg metal used for sponge production for it should not be a source for introducing any undesirable impurities.

The method for determination of silicon is based on the principle that small quantities of dissolved silicic acid react with a solution of ammonium molybdate in an acid medium resulting in the formation of yellow complex $H_4 [SiMo_{12}O_{40}]$. Since the photometric measurement based on this yellow complex is insensitive, a selective reduction of this complex with reducing agents like hydrazine sulphate, stannous chloride, 1-amino-2-naphthal-4-sulphonic acid, etc. produces a blue colour due to formation of silicomolybdenum blue complex of uncertain composition. The intensity of blue colour is proportional to the amount of silicon. In the present case, ascorbic acid was used for the reduction to molybdenum blue that exhibits maximum absorption at 815 nm thereby permitting its quantification.

The reaction conditions are adjusted so that only molybdosilicic acid and not the unreacted molybdic acid is reduced.

Also the sensitive and popular method due to reaction of ferrous ions in aqueous solution with O-phenanthroline with the formation of an orange red complex in the pH range of 2 - 9 that exhibits maximum absorption at 510 nm was applied for the determination of trace quantities of iron in above mentioned sample. Both the systems, i.e silicomolybdenum blue and ferrous-orthophenanthroline obey Beer-Lamberts Law in the concentration range normally encountered in the sample under discussion. Spectrophotometric measurements were carried out using 5 cm cells.

The results obtained by the proposed method are in good agreement with the results obtained by ICP-AES. As the proposed method meets the desired sensitivity, it is developed as an useful alternate method to ICP-AES. Replicate analysis performed (n=10) gives an RSD of $\pm 5\%$ of silicon and $\pm 10\%$ for iron.

Keywords: magnesium metal: Kroll's process: Magnesio-thermic reduction: Beer-Lamberts Law: molybdenum blue: ICP-AES: RSD.

ICP-53

ARE GRAVIMETRIC METHODS AS QUALITY CONTROL TOOLS NOT IMPERISHABLE?

U.Bharati Misra, K.Gopala Krishna, T.Amar Prakash and B.Narasimha Murty

Control Laboratory, Nuclear Fuel Complex, Hyderabad 500062, India.

Email: bnm@nfc.gov.in

Quality control measures implemented in a nuclear fuel bundle production plant demand analysis of materials at different stages of production including that of raw materials. This necessitates determination of analytical parameters in variety of samples. Wherever component of commerciality is involved in the sample, it becomes essential to employ the well established high precise technique like gravimetric method as an analytical tool for the day to day analytical work through the age old gravimetric techniques in general are time consuming. Nevertheless, it is always possible to incorporate certain modifications in the gravimetric method to make it relative less time consuming.

Gravimetric determination of zirconium involves precipitating zirconium quantitatively from large number of impurity elements using specific reagent such as mandelic acid [1]. The non-stoichiometry of zirconium tetramandelate due to presence of basic salts of varying composition [2] limits its usage as weighed form.

Procedure: 50g well homogenized as received washed dried frit sample is digested in 200 mL 60% nitric acid with continuous mechanical stirring on a water bath for 3 hours and the contents after cooling are made upto one litre with 2N nitric acid. To 50mL of the filtered solution in a Teflon beaker, 20 mL concentrated sulphuric acid and 5 mL 40% hydrofluoric acid are added and fumed on hot plate to dense

white fumes and after cooling the contents are diluted to 250 mL. The residue obtained after precipitation followed by filtration using 50mL aliquot of this solution is processed further by either Method A or B.

Method A: The residue is redissolved in minimum quantity of concentrated hydrochloric acid and 50 mL of 16% mandelic acid solution in hot condition is added and digested on water bath for one hour. The solution is filtered and residue is washed thoroughly with 2% mandelic acid and the residue is charred and ignited at 900°C for 2 hours. RSD (n=10) of this method: $\pm 0.23\%$.

Method B: The residue is redissolved in 30 mL of concentrated hydrochloric acid and the volume of the solution is made to about 50 mL by adding water and is boiled on hot plate. Now, 25 mL of 15% mandelic acid solution is added in a drop wise manner while the solution is continuously stirred manually with glass rod. The solution after cooling is filtered through Gooch crucible and the residue is thoroughly washed with 6% HCl saturated with mandelic acid and then the contents are dried at 110° C in an air oven for one hour and after cooling weight is recorded and content of ZrO₂ is calculated. RSD (n=10) of this method: $\pm 0.49\%$.

Method B has advantages like relatively more sample through put, less analysis time, no need of handling platinum ware and low cost per analysis. Obviously, it is the responsibility of the analyst to apply a given analytical method judiciously. Thus, even in the modern era, the age old gravimetric techniques continue to play vital role as tools in the hands of a judicious analyst for the purpose of quality control.

References

1. C.A. Kumins. Anal Chem 19, 376 (1947)
2. R.B. Hahn, E.S. Baginski. 14, 15 (1956)

ICP-54

DETERMINATION OF BORON AT TRACE LEVEL IN STAINLESS STEEL BY CARRIER DISTILLATION TECHNIQUE

A.K. Nayak, N. J. Lakshmi, Y.Balaji Rao* and R.B. Yadav

Control Laboratory, Nuclear Fuel Complex, Hyderabad 500062, India

Email: ybr@nfc.gov.in

Abstract

Nuclear Fuel Complex is engaged in production of nuclear fuel and structural materials for Pressurized Heavy Water Reactor (PHWR), Boiling Water Reactor (BWR), Proto type Fast Breeder

Reactor (PFBR) operating in India. Boron is a very critical element in all the materials of importance to nuclear power reactors owing to its high neutron absorption cross section ($\sigma_a = 755b$). Stainless steels are most preferred structural materials in FBR over alloys of Zirconium due to high burn-ups allowed in these reactors. A specification limit of less than 10 ppm is fixed in all types of steels except D-9 steels. In D-9 steels, a range of 10- 20 ppm of boron is allowed. Presence of boron has got pronounced effects on properties of steels especially hardness. The hardness is required for steels to sustain in reactor operating temperatures. Therefore, monitoring of boron in steels is mandatory under QC programme. Several methods are cited in literature for the determination of boron in steels. Among them, spectrophotometric method using curcumin as complexing agent is most sensitive. However, the quality of curcumin strongly influences the sensitivity and also reproducibility of this method. An ICP-AES method also exists for boron estimation in steels using most sensitive wavelength of 249.773 nm. At this wavelength, iron present in steels strongly interferes and thus needs separation of matrix prior to analysis. Instead of 249.773 nm, a vacuum UV line of 182.641 nm can also be tried for boron estimation. But, it requires continuous purging of high purity nitrogen for 6-8 hrs to remove traces of oxygen present in side the spectrometer thus making it unsuitable for an industrial lab. The matrix interference can be easily avoided by pyrohydrolysing the steels at high temperature followed by estimation of boron in collected solution employing Ion Chromatography (IC) coupled with spectrophotometer as detector. This method being a time consuming one, making it unsuitable for industrial labs where sample throughput is very high.

The present method describes the determination of boron in presence of matrix by emission technique using DC-Arc as excitation source. About 0.5 g of steel is dissolved in aqua-regia taken in a Teflon beaker (in order to avoid contamination from glass apparatus) followed by addition of 5 ml of 5% manitol ($C_{16}H_{14}O_6$) solution, which complexes with boron and thus does not allow boron to escape during the process. The resultant solution is transferred in to a silica dish and Fe as $Fe(OH)_3$ is precipitated with excess ammonium hydroxide solution. Subsequently the precipitate is dried and fumed on burner. The resultant residue after complete fuming is ignited at 600°C for 30 minutes in a muffle furnace to get respective oxides. The oxide is mixed with buffer in 4:1 proportion (buffer is a mixture of CuF_2 and C in 1:1 ratio) and ground perfectly. From the resulting mixture 35 mg of charge is loaded in an ultra pure carbon electrode and arced for 10 seconds using DC-Arc excitation source. Excitation conditions like current, electrode to electrode gap, duration of excitation, selection of buffer, sample to buffer ratio are optimized to get the best sensitivity and precision. By this technique it is possible to determine boron in steel at trace levels. A RSD of $\pm 10\%$ has been achieved in this method. The method is robust and can be used by industrial labs.

ICP-55

ESTIMATION OF CARBON AND SULPHUR IN MDU SAMPLES BY COMBUSTION METHOD USING CARBON SULPHUR ANALYSER

K.Vijayan, Y. Balaji Rao and R.B. Yadav

Control Laboratory, Nuclear Fuel Complex, Hyderabad 500062

Email: ybr@nfc.gov.in

Abstract

The present paper describes an analytical method followed at Control laboratory, Nuclear Fuel Complex (NFC) for the determination of carbon and sulphur content in Magnesium Diuranate (MDU) which is the starting material for the production of Nuclear grade Uranium Dioxide (UO_2) pellets. The knowledge of carbon and sulphur content in MDU is prerequisite since it poses process related problems during the conversion process of MDU to UO_2 powder. A high content of carbon in MDU causes frothing during its dissolution in nitric acid before the solvent extraction step. Likewise high sulphur in the form of sulphate affects the efficiency of solvent extraction where-in uranium forms complex with sulphate which will not be extracted into the aqueous phase. This leads to retention of high quantity of uranium in raffinate affecting the overall production of UO_2 powder. Hence, estimation of carbon and sulphur in MDU is vital for production process of UO_2 powder. The sample under test is burnt in a pre-degassed ceramic crucible with tungsten and iron as accelerators in a stream of oxygen. During this process, the carbon and sulphur present in the sample gets converted to their respective oxides and detected by a non-dispersive infrared absorption detector. The complete experimental details are discussed in the paper. Also the paper presents comparison of carbon and sulphur content in MDU samples obtained from Turamndih and Jaduguda mines. In addition, the effect of heating of MDU samples to different temperatures on their carbon and sulphur contents is also studied. The sulphur content as sulphate obtained from Carbon-Sulphur Analyzer (CSA) is compared with those obtained from Wave Length Dispersive X-Ray Fluorescence Spectrometer (WD-XRFS).

ICP-56

QUANTITATIVE ANALYSIS OF TRACE IMPURITIES IN IRON METAL POWDER USING FLAME-ATOMIC ABSORPTION SPECTROPHOTOMETRY

J.R. Jat, Y.Balaji Rao* and R. B. Yadav

Control Laboratory, Nuclear Fuel Complex, Hyderabad-500 062

E mail: ybr@nfc.gov.in

Abstract

Nuclear Fuel Complex (NFC) is responsible for fabrication of fuel and reactor core components required for operating the nuclear power reactors in India. Structural materials used in water cooled reactors must possess a combination of high corrosion resistance and low neutron absorption cross section. Alloys of zirconium meet all these requirements and hence preferred a choice for making structural materials. In order to ensure adequate mechanical strength to components in the reactor core and also for dependable corrosion resistance at elevated temperatures and pressurized water environment, zirconium has to be alloyed with certain alloying constituents like chromium, nickel, iron and tin to get desirable properties. That is how alloys of zirconium have become indispensable to present day CANDU type of reactors as structural components and as fuel cladding material.

NFC produces various types of reactor components such as fuel clad, pressure tubes, calandria tubes, garter springs etc, apart from different reactivity mechanisms. Most of these components are made up of different types of zirconium alloys like Zircaloy-2, Zircaloy-4 except pressure tubes (coolant tubes), which are produced using Zr-2.5% Nb alloys and Zr-2.5%Nb-0.5%Cu for garter springs.

The specifications with respect to alloying elements in alloys of zirconium are given in table 1.

Table 1: Composition of Zirconium alloys

Element	Zr-2 (in %)	Zr-4 (in %)
Cr	0.05 - 0.15	0.07 – 0.13
Fe	0.07 – 0.20	0.18 – 0.24
Ni	0.03 – 0.08	70 ppm (max)
Sn	1.2 – 1.7	1.2 – 1.7

The alloying constituents of high purity grade are purchased from private suppliers and the purity of the supplied material is to be ensured both from the cost point of view as well as the integrity of the material since it should not become a source for introducing any undesirable impurity in Zircalloys and affect its use in the reactors. Thus analysis of impurities in alloying constituents becomes an essential part of the quality assurance programme. The present paper deals with the chemical characterization of Iron metal powder to be used as alloying element in formation of Zircaloy.

The specifications with respect to impurities in iron metal powder are given in table 2.

Table 2: Specifications of impurity elements in Fe powder

Element	Maximum value (in %)	Element	Maximum value (in %)
Al	0.30	O	0.50
Bi	0.01	Pb	0.05
C	0.05	S	0.01
Cu	0.05	Sb	0.01
N	0.02	Si	0.20

Of these impurities listed Al, Cu, Pb and Si are being estimated by Flame-AAS.

The present paper describes a method for analysis of iron powder for these elements. Atomic Absorption Spectrophotometer (Model: Analytik Jena Vario6, Germany) is employed for the analysis. All the experimental conditions such as flame, selecting wavelength, HCL current etc., along with suitable sample solution preparation are optimized so as to get better sensitivity. In order to take care of matrix suppression, standard addition method was resolved. A linear calibration curve between absorbance and concentration of standard added has been obtained for all the elements of interest. A RSD of $< \pm 10\%$ has been achieved for all the elements.

ICP-57

COMPOSITIONAL CHARACTERIZATION OF STAINLESS STEEL USING WDXRF SPECTROMETRY

Rugmini Kaimal and Anita Kadam

Atomic and Molecular Physics Division , B.A.R.C., Trombay, Mumbai 400 085,

email: rugmani@barc.gov.in

Abstract

Stainless steel of varying specifications is in increasing demand in the construction of nuclear power reactors and also important from the metallurgical point of view. Presence and concentration of major and minor alloying elements (viz. Ni, Cr, Mn etc.) play the vital role in deciding the suitability of

stainless steel for any specific purpose. Conventional chemical methods of analysis are laborious, cumbersome and invariably require distinct analytical procedure for determining individual alloying element. Spectrometric methods such as ICP-AES [1] are available but the sample preparation by dissolution is tedious and time consuming. X-ray fluorescence method [2] which is rapid and non destructive is extremely useful in the quality control of steel industry because of its highly precise and accurate results.

In this paper we discuss standardization of a wavelength dispersive X-ray fluorescence (WDXRF) method for the determination of Ni, Cr, Mn and Si in stainless steel using Philips PW 2400 X-ray spectrometer. Samples in the form of discs of 30 mm diameter and thickness of a few mm – 20mm are loaded in the sample holders of the equipment after surfacing to a fine finish. The concentration of the element in the samples is found out from the intensity of their characteristic X-rays. Major problem of matrix effects, mainly line absorption, enhancement effect and spectral superposition are minimized by using a set of standards of known concentration with matching matrix composition. The calibration curves are obtained by plotting fluorescent intensity against concentration of standards. Calibration curves obtained using the procedure is shown in fig. 1-4. The standards used in this work are from National Bureau of Standards (NBS, SRM Group III, for Stainless steel). Accuracy of the method is checked by analysis of samples of known concentration. The precision of this method is determined by calculating standard deviation of 15 repeated measurements of average background and net peak intensities. The results are shown in Table 1.

In conclusion, we have developed and presented here WDXRF technique, which finds application in analysis of stainless steel for nuclear power plants. The method is simple fast and accurate.

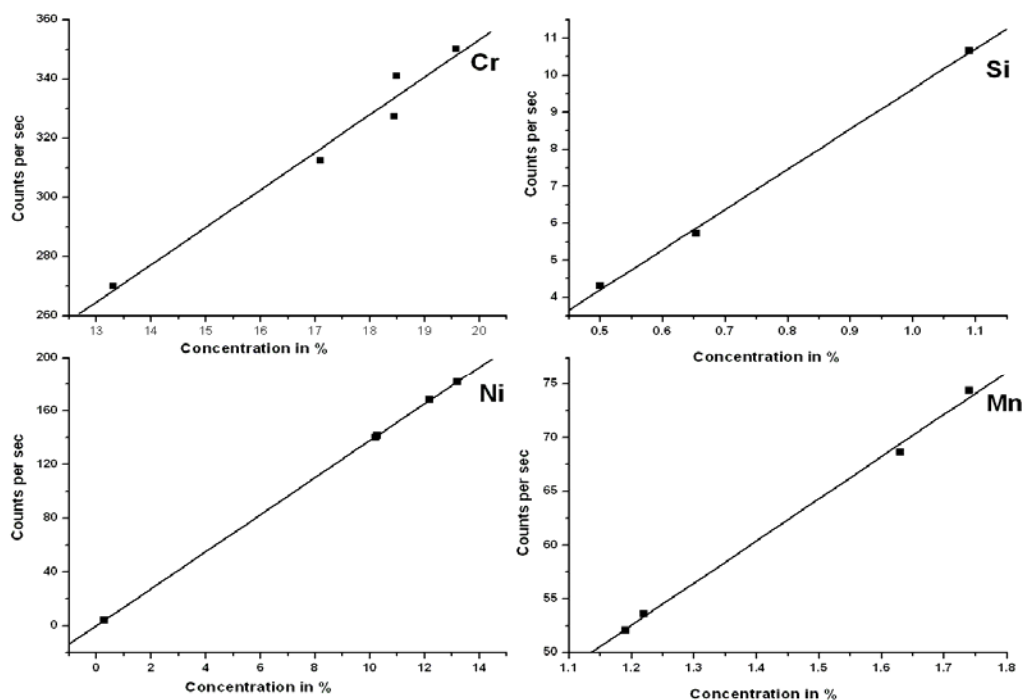


Fig. 1: Calibration Curve

Table I: Concentration of each element in the standard and percentage standard deviation.

Std. SS SRM Group III Code No.	Ni		Cr		Mn		Si	
	Conc. [§]	% RSD	Conc.	% RSD	Conc.	% RSD	Conc.	% RSD
1152	10.21	0.325	18.49	0.158	1.19	0.947	0.654	0.584
1154	10.25	0.172	19.58	0.117	1.74	0.388	1.09	2.45
1155	12.18	0.130	18.45	0.159	1.63	0.307	0.50	1.46
1185	13.18	0.248	17.09	0.108	1.22	0.70	0.40	1.3
D-845	0.28	1.02	13.31	0.27	0.77	1.53	0.52	2.69

[§]Conc. of standards – Chemical composition (nominal wt percent)

References

1. S.S. Deshpande, P.B. Patil, Omana Narayanan and P.P. Khanna, BARC Report /E/014, 2002.

2. R.M. Agrawal, P.P. Khanna, BARC Report, 699, 1973.

ICP-58

SOLAR PHOTOCATALYTIC DEGRADATION OF RESORCINOL OVER B-DOPED ZINC OXIDE

Ashokrao B. Patil^a, Kashinath R. Patil^b, Malhari N. Raste^a and Satish K. Pardeshi^{a,*}

^a Department of Chemistry, University of Pune, Ganeshkhind, Pune-411007 (INDIA)

^b Center for Materials Characterization, National Chemical Laboratory, Pune-411008 (INDIA)

* Corresponding author. Tel.: +91 020 25601394 Extn. 514;

Fax: +91 020 25691728.

E-mail: skpar@chem.unipune.ac.in (S.K.Pardeshi)

Photocatalysis is a promising technique for environmental detoxification, due to its ability to destroy a wide range of pollutants at ambient conditions. TiO₂ is the most commonly used as photocatalyst under UV light [1]. Zinc oxide is a better option for TiO₂ because of its higher response towards solar energy [2-5]. B-doped zinc oxide powders have been synthesized by mechanochemical method and characterized by TG-DTA, XRD, XPS, SEM, EDXS, and PL spectra. X-ray diffraction data suggest that the B-doped ZnO crystallites have hexagonal wurtzite structure and the incorporation of B expands the lattice constants of ZnO. PL spectra of B-doped ZnO samples showed luminescence peaks in the UV and green emission region.

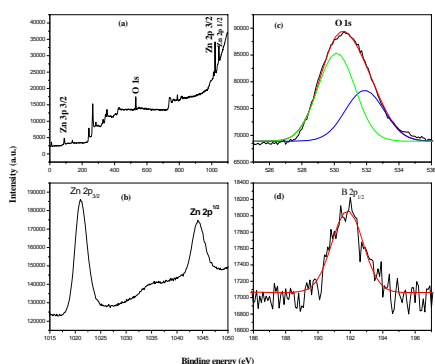
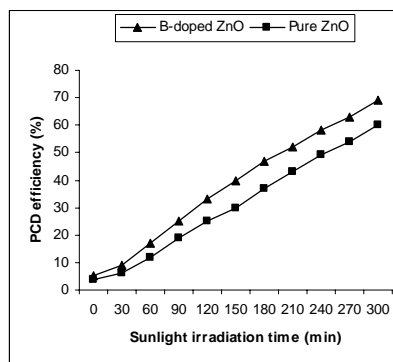


Fig.1 XPS of B-doped ZnO



3.

Fig.2 PCD of resorcinol over B-

doped ZnO

Whole scanning XPS spectrum of B-doped ZnO is shown in **Fig.1a**. The XPS peaks located at 1022eV and 1045eV are assigned for electronic states of Zn 2p_{3/2} and Zn 2p_{1/2} respectively (**Fig.1b**). **Fig.1c** shows O1s XPS spectrum, the peak at 530eV was attributed to O²⁻ ions of ZnO, while another at 531.5eV is usually associated with the adsorbed O₂. In the **Fig.1d**, the

peak positioned at 192eV was assigned to the B 2p_{1/2} electronic state. Thus the XPS data supports the incorporation of B in to the ZnO. Energy dispersive X- ray spectrum (EDXS) of B-doped ZnO shows peaks corresponding to Zn, O and B. No trace amount of other impurities could be seen in the detection limit of the EDXS which also supports the doping of boron in ZnO.

Photocatalytic activity of B- doped ZnO was checked by means of oxidative photocatalytic degradation of resorcinol. Complete mineralization of resorcinol was confirmed by chemical oxygen demand (COD) reduction method [6]. The photocatalytic degradation (PCD) efficiency was calculated from the following expression (1).

$$\eta = \frac{(\text{COD}_i - \text{COD}_t)}{\text{COD}_i} \times 100 \quad (1)$$

Where, η = Photocatalytic degradation efficiency, COD_i = Initial chemical oxygen demand, COD_t = Chemical oxygen demand at time t. The average photon flux calculated by ferrioxalate actinometry [7] for sunlight was found to be 1.7×10^{-7} Einstein $\text{s}^{-1}\text{cm}^{-2}$.

Fig. 2 shows PCD of resorcinol over B-doped ZnO in comparison to bare ZnO. The 70% PCD of 150ppm resorcinol was achieved over 250mg / 100mL loading of B-doped ZnO at its natural pH within 5h irradiation of sunlight. The rate constants of PCD of resorcinol over B-doped ZnO is greater ($3.4 \times 10^{-3} \text{ h}^{-1}$) than that over pure ZnO ($2.5 \times 10^{-3} \text{ h}^{-1}$). Hence, the solar PCD efficiency of B-doped ZnO was found to be greater than that of pure ZnO. PCD of resorcinol follows first order reaction kinetics. Activity of recycled B-doped ZnO was found to retain even after fifth PCD experiment.

[1] D. Chatterjee, S. Dasgupta, J. Photochem. Photobiol. C: Photochem., **6**, 186–205, (2005).

[2] S.K. Pardeshi, A.B. Patil, Solar energy, **82**, 700-705, (2008).

[3] B. Dindar, S. Icli, J. Photochem. Photobiol. A: Chem., **140**, 263–268, (2001).

[4] S.K. Pardeshi, A.B. Patil, J. Hazard. Mat., **163**, 403- 409, (2009).

[5] S.K. Pardeshi, A.B. Patil, J. Mol. Catal. A: Chem., **308**, 32–40, (2009).

[6] J.T Bellaire, G.A Parr-Smith, Standard methods for the examination of water and wastewater, seventeenth ed. Am Public Health Association, Washington D C, 1985.

[7] C.G. Hatchard, C.A. Parker, A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer, Proc. R. Soc. London, A235, 518, (1956).

AN IMPROVED PROCESS FOR SYNTHESIS OF DIALKYL-2,6 - DIMETHYL-4-ALKYL / ARYL-3,5- PYRIDINE DICARBOXYLATES USING $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ IN AIR

D. D. Kumbhar, B.D.Jadhav, S. K. Pardeshi*

Department of Chemistry, University of Pune, Ganeshkhind, Pune-411007 (INDIA)

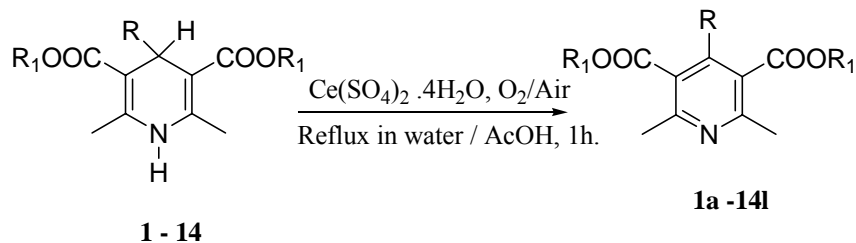
*Corresponding author.

Tel.: +91 020 25601225 Extn. 514.

Fax: +91 020 25691728.

E-mail: skpar@chem.unipune.ac.in (S.K.Pardeshi)

14 compound of dialkyl-2, 6-dimethyl-4-alkyl/aryl-3, 5-pyridine dicarboxylates were synthesized by using $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in air. The products **7g**, **8h**, **9i**, and **10j** are successfully synthesized as solid fine crystals for the first time. The reversible conversion of Ce^{3+} to Ce^{4+} due to oxygen present in air plays an important role in synthesis of these products. The workup procedure is very simple and provides yields greater than 90%, which appears to be limited only by the purity of the starting material and the efficacy



of the isolation procedure.

Scheme 1

Synthesis of dialkyl-2, 6 - dimethyl-4-alkyl / aryl-3, 5- pyridine dicarboxylates has gained interest in recent years due to the fact that these compounds based antihypertensive drugs (calcium antagonists) are oxidatively converted to pyridine derivatives by cytochrom P-450 in liver [1].Dialkyl-2, 6 - dimethyl-4-alkyl / aryl-3, 5- pyridine dicarboxylates (DHPs) have been extensively utilized as the analogs of NAD(P)H co-enzymes to study the mechanism and synthetic potential of various redox processes[2,3]. The 1, 4-DHP based drugs such as Nifedipine and Niguldipine have been widely used in the treatment of hypertension and angina pectoris. These compounds bind to specific receptors and are Ca^{2+} channel blockers for the treatment of cardiovascular disease [4-6].Consequently this oxidation reaction continues to attract the attention of researchers for the discovery of milder and general procedure applicable to a wide range of 1, 4-DHP. Several reagents have been used for the oxidation of dialkyl-2, 6 - dimethyl-4-alkyl / aryl-3, 5- pyridine dicarboxylates which includes HNO_3 , [4] KMnO_4 , [7].etc.

In the present work, synthesis of dialkyl-2, 6 - dimethyl-4-alkyl / aryl-3, 5- pyridine dicarboxylates using $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in air by refluxing in 10mL water and addition of 2mL acetic acid is done. Here water acts as solvent for the reaction. The unique role of acetic acid is in promoting oxidation which may be tentatively attributed to appreciable solubility of ceric sulfate tetrahydrate in water and generation of the active oxidant species.

References:

- [1] F. P. Guengerich, W.R. Brian, M. Iwasaki, M. A. Sari, C. Baarnhielm, P. Berntsson, *J. Med. Chem.* **34**, 1838, (1991).
- [2] D. M. Stout, A. I. Meyers, *Chem. Rev.* **82**, 223, (1982).
- [3] R.J. Kill, D.A Widdowson, In *Bioorganic Chemistry*; van Tamelen, E. E., Ed.; Academic Press: New York, 1978, Vol. 4, pp 239–275.
- [4] R. H. Bocker, F. P. Guengerich, *J. Med. Chem.* **29**, 1596, (1986).
- [5] X. Y. WWI, A. Rutledge, D. J. Triggle, *Mol Pharmacol*, **35**, 541, (1989).
- [6] M. M. Sadeghi, I. Mohammadpoor-Baltork, H. R. Memarian, S. Sobhani, *Synth. Commun.* **30(9)**, 1661, (2000).
- [7] J. J. Vanden Eynde, R. Orazio, Y. Van Haverbeke, *Tetrahedron* . **50**, 2479, (1994).

ICP-60

SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF BaFe_2O_4 COMPLEX OXIDE: AN EFFICIENT CATALYST FOR SELECTIVE OXIDATION OF STYRENE

Ravindra Y. Pawar Baliram Y. Waghmare and Satish K. Pardeshi *,

Department of Chemistry, University of Pune, Ganeshkhind,

Pune-411007 (INDIA)

* Corresponding author. Tel.: +91 020 25601395 Extn. 514;

Fax: +91 020 25691728.

E-mail: skpar@chem.unipune.ac.in (S.K.Pardeshi)

Abstract

Alkaline earth metal (AEM) ferrites have considerable attention due to their potential application mainly due to its low cost, high saturation magnetization, high Curie temperature and high coercivity associated with excellent chemical stability high mechanical durability, and resistant to corrosion [1]. The AEM ferrite like CaFe_2O_4 has also been employed as heterogeneous catalyst for selective oxidation of styrene [2]. In the present study BaFe_2O_4 catalyst is synthesized by citrate gel method. The precursor and oxide are well characterized by various techniques such as TG-DTG, FT-IR, X-ray diffraction, SEM, and X-ray fluorescence. The crystallization temperature of the spinel particle prepared by citrate gel method is 600°C which is lower than that of ferrite prepared by other methods. BaFe_2O_4 catalysts prepared by citrate gel method shows high activity for styrene oxidation in presence of H_2O_2 (30%) as an oxidizing agent. GCMS analysis revealed that, during the course of reaction the oxidative cleavage of C=C double bond of styrene takes place selectively to give benzaldehyde up to 88 mol% as the major whereas phenyl acetaldehyde 12mol% minor products. The selective oxidation of styrene to benzaldehyde is optimized at 50°C for 18 h in water as solvent over 0.1g of catalyst.

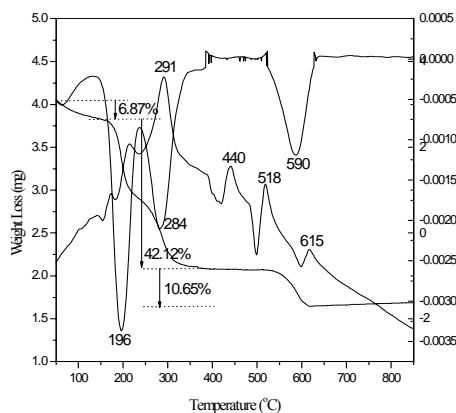


Fig.1. TG-DTG-DTA curve of barium iron citrate precursor

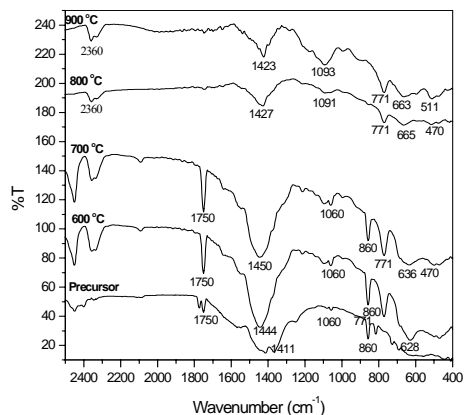


Fig.2. FTIR spectrum of precursor and BaFe_2O_4 calcined at different temperature

Table 1 Elemental analysis of BaFe_2O_4 catalyst by X-ray fluorescence method in percentage by weight.

Barium		Iron	
Calculated	Observed	Calculated	Observed
39.1	38.4	28.8	31.2

1. Catalytic activity studies:

The catalytic activity of the synthesized catalyst is tested by using selective oxidation of styrene as a model reaction. This reaction is of significant importance in the fine chemicals and pharmaceutical industries. While, the products represent important intermediates for the preparation of various other compounds [3, 4]. Some strong oxidants such as KMnO_4 , CrO_3 , and HNO_3 [5, 6] were applied traditionally to the oxidation of various substrates, which might result in much serious pollution and some potential risks in the process of operation. In terms of atom efficiency and environment friendly, after oxygen, aqueous hydrogen peroxide (30% H_2O_2) is a very attractive oxidant for industrial applications since water is the only by-product, and it is easy to deal with after reactions.

2. Optimization of reaction conditions:

The conditions for maximum conversion of styrene as well as selectivity for desired product have been optimized by varying different parameters such as temperature, styrene: H_2O_2 molar ratio, amount of catalyst, reaction time, ultrasonication time etc. On oxidation, styrene gives benzaldehyde as major product while, phenyl acetaldehyde as minor product which are widely used as solvents, perfumes or flavoring agents or as intermediate in manufacture of plastics, dyes and pharmaceuticals.

2.1. Effect of time

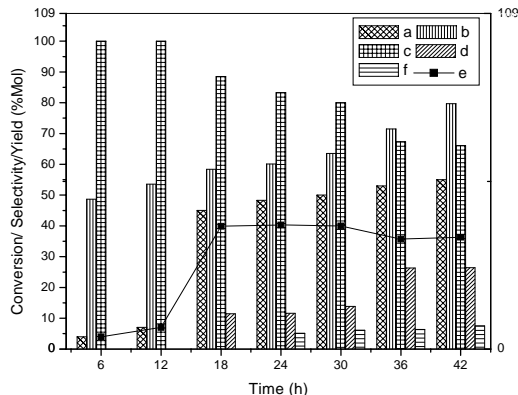


Fig. 3 Effect of reaction time on conversion and product selectivity

2.2. Influence of temperature

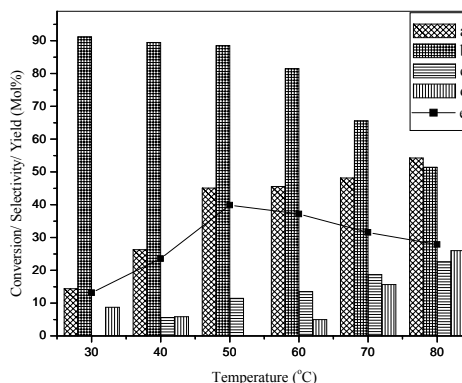


Fig. 4 Effect of reaction temperature on conversion and product selectivity

References:

- [1] X. Liu, J. Nang, L.M. Gan, S.C. Ng, J. Ding, J. Magn. Mater. **184**, 344, (1998)
- [2] Satish K. Pardeshi, Ravindra Y. Pawar, J. Mater. Res. Bull. **45**, 609-615, (2010)
- [3] G.A. Mirafzal, A.M. Lozera, Tetrahedron Lett. **39**, 7263-7266, (1998)
- [4] J.D. Lou, W.X. Lou, Synth. Commun. **27**, 3697-3699 (1997)
- [5] K. Sato, M. Aoki, T. Hashimoto, R. Noyori, J. Org. Chem. **61**, 8310- 8311 (1996)
- [6] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Panyella, R. Noyon, Bull. Chem. Soc. Jpn. **70**, 905 (1997)

ICP-61

VALIDATION OF GC-MS/MS METHOD FOR MULTI RESIDUE ANALYSIS OF PESTICIDES IN MANGO

Deepa G.T., Mahadev B. Chetti*, M.C.Khetagoudar P.T.Goroji., Dinesh B.K.

*Corresponding author : Dean (Agri.), University of Agricultural Sciences, Dharwad – 580 005, Karnataka, India,

Cell : 094484 95309, Fax : +91-836-2792180, E-mail address : mbchetti_uas@rediffmail.com

ABSTRACT

A gas chromatographic –tandem quadruple mass spectrometric [GC-MS/MS] method for analysis of multi class [Organochlorines, Organophosphorus, Pyrethroids and Triazoles] pesticide residues of mango has been developed and validated. Mass spectrometry is a very sensitive, selective technology for both multiresidue and trace level identification of wide range of pesticides. The extraction of pesticide residues was carried out by dispersive solid phase extraction (dSPE) method, is based on the solvent extraction of homogenized mango sample by acetonitrile added to the 50 ml tube containing sodium acetate and magnesium sulphate. Co-extractives were removed with primary secondary amine (PSA) and graphitized carbon black (GCB), the samples were further cleaned up by using 0.2 µm filter paper. Identification of the compound done by matching the full-scan spectra with the corresponding NIST library with the match threshold of > 80%. Confirmation criteria of the pesticides were based in the 2002/657/EC European Commission Decision. The method was validated by fortified mango samples at different concentration levels. Average recoveries ranged from 80-100% with Relative standard deviation [RSD] between 3.9 % and 13.2 % . Performance characteristics linearity, detection limit [LOD], quantification limit [LOQ], precision and recoveries were studied.

Key words: GC-MS/MS; Multiresidue; Mango; LOD; LOQ; dSPE

ICP-62

INTERFERENCE OF DIFFERENT IONIC SPECIES ON THE ANALYSIS OF PHOSPHATE IN HLW USING SPECTROPHOTOMETER

P.K.Mishra, D.E.Ghongane, T.P.Valsala, M.S.Sonavane, Y.Kulkarni, and R.D.Changrani.

Waste Management Facilities, Bhabha Atomic Research Centre, India, Tarapur – 401 504

e-mail tpvalsala@gmail.com

Introduction:

During reprocessing of spent nuclear fuel by PUREX process different categories of radioactive liquid wastes like High Level (HL), Intermediate Level (IL) and Low Level (LL) are generated [1,2]. Different methodologies are adopted for management of these wastes [3]. Since PUREX solvent (30% Tri butyl phosphate-70% Normal Paraffin Hydrocarbon) undergoes chemical degradation in the highly acidic medium of dissolver solution [4], presence of phosphate in the waste streams is inevitable. Since higher concentrations of phosphate in the HLW streams will affect its management by vitrification, knowledge about the concentration of phosphate in the waste is essential before finalising the glass composition. Since a large number of anionic and cationic species are present in the waste, these species may interfere phosphate analysis using spectrophotometer. In the present work, the interference of different anionic and cationic species on the analysis of phosphate in waste solutions using spectrophotometer was studied.

Experimental:

Simulated radioactive waste solution was prepared by using appropriate chemicals. The composition of the simulated waste is given in Table-1. Determination of phosphate was carried out by phosphovanado molybdate complex method using spectrophotometer [5]. Calibration of the spectrophotometer was carried out using spectroscopic solution of phosphate. Interference due to individual elements was studied by measuring the phosphate concentration in the presence of corresponding ions. The concentration of various ions is selected in accordance with their concentration in the waste solution. To see the combined interference of all the ions, analysis of the simulated waste solution was also carried out.

Results and discussion:

The calibration curve for the phosphate analysis is given in Figure-1. The interfering ions taken for study and their concentration are given in Table-2. Higher concentrations for different ions are selected than their presence in the HLW solutions. The actual concentration of phosphate in different solution and the analysed value are also presented in Table-2. From the Table it can be seen that the error in the analysis due to the interference are within the acceptable limit (<5%) for cations like Na^+ , K^+ , Cs^+ , Al^{+3} , Fe^{+3} , Mn^{+2} ,

Ni^{+2} , Mo^{+6} , Zr^{+4} and U^{+6} . In the case of Cr^{+6} , about 10% error is observed at the concentration of 20ppm. However the error due to 10ppm concentration is within the limit. The error due to the anions studied is also within the limit. The error in the analysis of phosphate in the simulated waste is about 5% and is acceptable. Here the positive and negative errors due to different ions may be getting nullified.

Conclusion:

During the analysis of phosphate in the HLW by phosphovanado molybdate complex method using spectrophotometer, the positive and negative errors due to the interference of different ions are getting nullified. Hence phosphate in the HLW can be analysed by phosphovanado molybdate complex method within the error limit of 5%.

References:

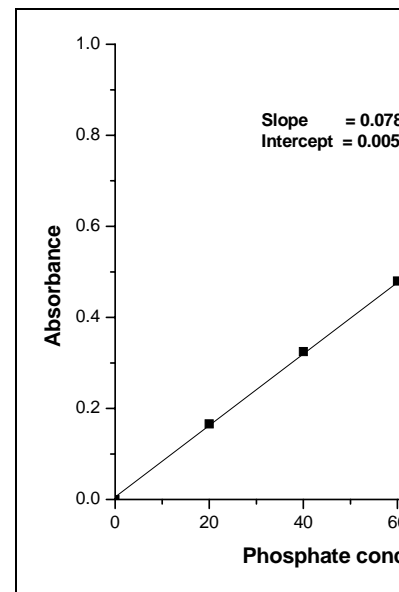
1. A. Ramanujam, Separation Science and Technology, **34**, p1717-28, (1999).
2. IAEA Technical Report Series, **No.236** IAEA, Vienna, Austria, 1984
3. K.Raj, K.K.Prasad, N.K.Bansal, Nucl. Engg. Design, **236**, 914 (2006).
4. J.C.Neace, Separation science and Technology, **18**, p.1581-1594 (Nov 1983).
5. G.H.Jeffery, J.Bassett, J.Mendham, R.C.Denney, Vogel's Text book of quantitative chemical analysis, **Sixth edition**, p. 700.

Table-1: Composition of Simulated waste

Sl.No	Cations/ anions	Conc., ppm
1	Na^{+}	80
2	K^{+}	40
3	Cs^{+}	20
4	Al^{+3}	20
5	Fe^{+3}	60
6	Mn^{+2}	40
7	Ni^{+2}	25
8	Cr^{+6}	10
9	Mo^{+6}	20
10	Zr^{+4}	20
11	U^{+6}	40

12	Cl ⁻	40				
13	(SO ₄) ⁻²	40				
14	(PO ₄) ⁻³	100	Sl.No.	Cation/an	Conc. of Cation/ anion, ppm	* Observed conc. of (PO ₄) ⁻³ , ppm
				ion		% error
			1	Na ⁺	100	98.25
			2	K ⁺	100	97.87
			3	Cs ⁺	20	100.80
			4	Al ⁺³	20	99.82
			5	Fe ⁺³	100	96.85
			6	Mn ⁺²	100	98.38
			7	Ni ⁺²	25	97.27

Figure-1:
curve for
analysis

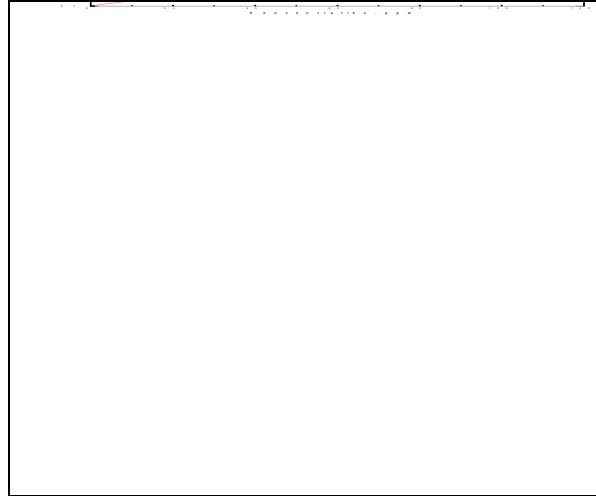


Calibration
phosphate

Table-2: Interference of cations/ anions on phosphate analysis

8	Cr ⁺⁶	20	110.30	10.3
9	Cr ⁺⁶	10	102.80	2.8
10	Mo ⁺⁶	20	96.00	-4.0
11	Zr ⁺⁴	20	96.62	-3.38
12	U ⁺⁶ .	100	96.70	-3.3
13	Cl ⁻	100	99.27	-0.73
14	(SO ₄) ⁻²	100	97.87	-2.13
15	Simulated waste	See table-1	104.92	4.9

* Actual concentration of phosphate in solution is 100.00ppm



ICP-63

**DETERMINATION OF DEGRADED PRODUCTS OF TBP IN THE SODIUM
CARBONATE WASTE SOLUTIONS OF PUREX PROCESS**

**D.A. Thakur, V.S.Pardeshi, R.K.Sah, N.L Sonar, T.P. Valsala, Y.Kulkarni and
R.D.Changrani**

Waste Management Facilities, Bhabha Atomic Research Centre, India, Tarapur – 401 504

e-mail tpvalsala@gmail.com

Introduction:

PUREX process is widely employed for reprocessing of spent nuclear fuel using dilute TBP (30% Tributyl phosphate-70% normal paraffin hydrocarbon). During the course of its use, the PUREX solvent undergoes chemical and radiolytic degradation [1]. Major degradation product is dibutyl phosphate (DBP). To purify the solvent from degraded products, sodium carbonate wash treatment is applied periodically. The resultant carbonate wash waste falls under the category of Intermediate Level radioactive liquid Waste (ILW). During the conventional IX treatment [2] of this ILW it was observed that at the carbonate destruction step the DBP in the waste is forming a sticky and difficult to handle yellow mass with the uranyl ions. Major portion of alpha and some amount of beta activity are associated with this sticky mass. Alternate method of direct cementation/ polymerization and disposal in the NSDF is not possible for this ILW due the presence of high alpha activity. Hence remediation of this ILW prior to IX treatment was tried and various schemes were developed at different laboratories [3,4,5]. A new treatment scheme involving partial carbonate destruction followed by alkali precipitation of uranyl ions

was worked out in our laboratory. Flow sheet for the new scheme is presented in Figure-1. Present work details the analysis of degraded products of TBP in different streams of the new treatment scheme.

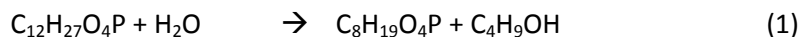
Experimental:

The study was carried out using actual radioactive liquid waste. Samples from selected step of the remediated scheme (Figure-1) were collected to determine the amount of PUREX solvent degraded products. The analysis was carried out by different methods.

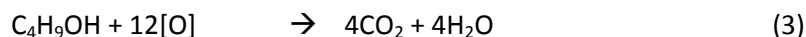
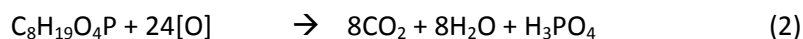
1. Phosphate analysis: Determination of organic phosphate in the samples was carried out by phosphovanado molybdate complex method using spectrophotometer [6]. For this the organic phosphates in the sample are converted into inorganic phosphates by giving perchloric acid treatment. The inorganic phosphates in the sample without perchloric acid treatment were considered as blank value.
2. Chemical oxygen demand (COD) determination: Standard open reflux method involving acidic dichromate oxidation was used for COD determination [7].
3. In another experiment, the supernatant after alkali precipitation (sample-2) was acidified to 1M acid and the volume of degraded products separated at the top was measured.

Results and discussion:

Degradation of TBP can be given as



Complete oxidation of DBP and butanol are given as



Phosphate analysis of the alkaline ILW (sample-1), supernatant after alkali precipitation (sample-2) and the dissolved uranyl precipitate (sample-3) was carried out. Concentration of degraded products namely DBP in these samples was calculated using phosphate concentration and equation-2. Oxygen requirement for total oxidation of organics in these samples was measured by COD determination. Using the COD data and the theoretical oxygen requirement for complete oxidation of DBP (calculated using equation-2&3), the concentration of DBP in the samples was calculated. The results are given in Table-1.

Results from phosphate analysis correspond to the organophosphate (DBP) concentration only. Where as, results of COD measurements correspond to the total degraded products in the sample namely DBP and butanol. Hence to calculate the COD value corresponding to DBP, the COD value of butanol has to be subtracted from total COD value. For this at first the concentration of butanol was calculated using

the phosphate concentration and equation-1. Then the COD value corresponding to butanol concentration was calculated using equations-3. The value obtained was subtracted from total COD value and the concentration of DBP was calculated. It can be seen from the table that these DBP concentrations are comparable with that obtained by phosphate analysis. The difference of about 15-20% in the values may be due to the contribution of small amounts of other degraded products.

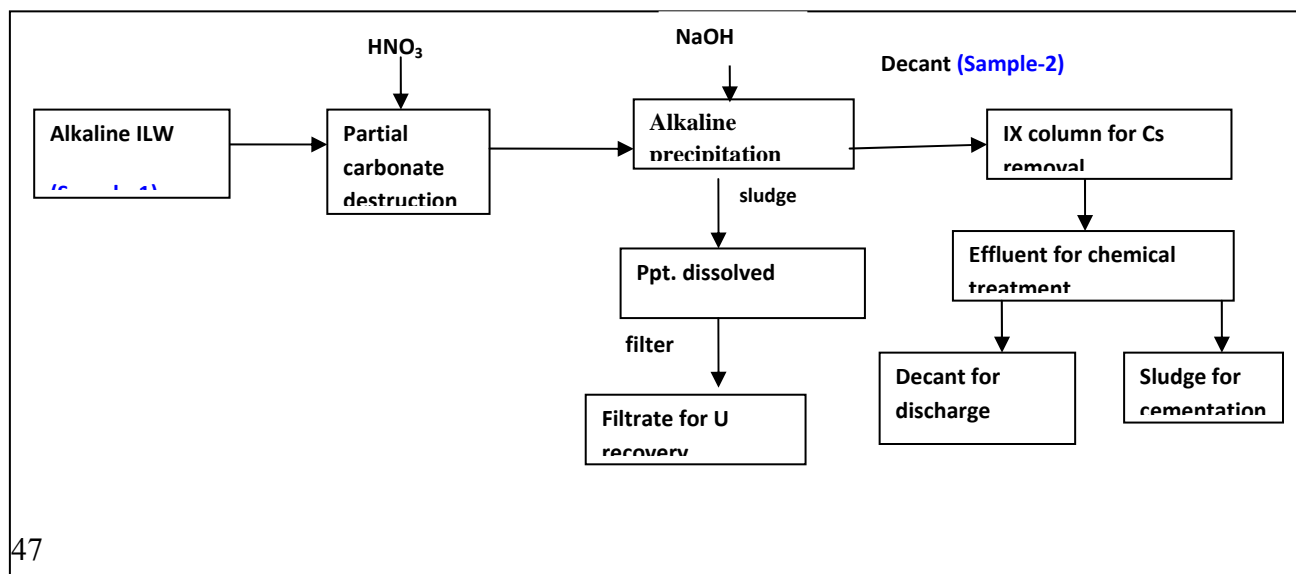
The amount of degraded products separated after acidification of sample-2 was found to be about 2.3vol%. After converting into wt %, the value (2.6 wt %) is comparable with that obtained by COD determination.

Conclusion:

Concentration of DBP determined by phosphate analysis and total oxygen demand determination are comparable. The higher value (15-20%) in the case of COD determination method is due to the contribution of small amounts of diluent degraded products. The total degraded products of TBP measured by COD method and by the amount of organic layer separated are also comparable.

References:

1. G.F.Vandegrift, Science and Technology of Tributylphosphate: **Volume I** Synthesis, Properties, Reactions and Analysis, Ed. W. W. Schulz, J. D. Navratil, A. E. Talbot, 127-130, CRC Press, Inc., Boca Raton, FL (1984).
2. R.G.Yeotikar, C.P.Kaushik, J.Gabriel, **NUCAR-95**, 429-430 (1995).
3. D.E.Ghongane, P.K. Mishra, T.P.Valsala, M.S.Sonavane, Y.Kulkarni, R.D.Changrani, proc: **SESTEC-2008**, 143-144 (2008).
4. D.K.Pant, K.K.Gupta, P.G.Kulkarni, P.B.Gurba, M.S.Sonavane, P.Janardan, R.D.Changrani, P.K.Dey, proc. **NUCAR-2009**, 177-178 (2009).
5. C.Srinivas, J.L.Goswami, P.K.Wattal, P.K.Mishra, T.P.Valsala, M.S.Sonavane, Y.Kulkarni, R.D.changrani, K.Raj, BARC report, **BARC/2010/1/005** (2010).
6. G.H.Jeffery, J.Bassett, J.Mendham, R.C.Denney, Vogel's Text book of quantitative chemical analysis, Sixth edition, p. 700.
7. G.H.Jeffery, J.Bassett, J.Mendham, R.C.Denney, Vogel's Text book of quantitative chemical analysis, sixth edition, p. 452.



Sl.No.	Sample code	COD measurement			Phosphate
		COD, g/L	Conc. degraded products, g/L	Conc. DBP, g/L	Conc. DBP, g/L
1	Sample-1	50.2	27.5	19.2	16.2
2	Sample-2	48.1	26.4	18.9	14.9
3	Sample-3	1.4	0.8	0.5	0.6

Table-1: Concentration of degraded products in different streams

ICP-64

PRODUCTION OF ETHANOL FROM ENZYMATIC HYDROLYSATES OF CORN AND SORGHUM FIELD WASTES EMPLOYING *PACHYSOLEN TANNOPHILUS* AND *SACCHAROMYCES CEREVISIAE* FOR SUSTAINABLE MANAGEMENT OF ENVIRONMENT

C. Sathesh-Prabu and A. G. Murugesan

SPK Centre of Excellence in Environmental Sciences

Manonmaniam Sundaranar University

Alwarkurichi - 627 412. Tamil Nadu

Abstract

The production of fuel alcohol from renewable resources has received considerable interest in recent years. Lignocellulosic biomass such as agricultural residues can be used as a feedstock for producing bioethanol to avoid conflicts between human food use and industrial use of crops. In this study, we demonstrate that the corn and sorghum field WASTES could be used to produce fuel grade ethanol. The alkaline treatment of 3% AND 2% NaOH removed maximum amount of lignin from corn and sorghum field wastes respectively. Cellulase enzyme treatment was followed to release reducing sugars from the raw materials. Yeast strains *Saccharomyces cerevisiae* (MTCC 173) and *Pachysolen tannophilus* (MTCC 1077) were used in the experiment. pH and temperature were optimized for the

better growth of *S. cerevisiae* and *P. tannophilus*. Maximum of 66 g L⁻¹ and 59 g L⁻¹ of ethanol yield were obtained by *P. tannophilus* and *S. cerevisiae* from CC, respectively. In case of CS, *P. tannophilus* and *S. cerevisiae* recorded the maximum of 63 g L⁻¹ and 55 g L⁻¹ of ethanol yield. Maximum of 68 g L⁻¹ and 56 g L⁻¹ of ethanol yield were obtained by *S. cerevisiae* and *P. tannophilus* from sorghum stover, respectively. Respiratory deficiency and ethanol tolerance of the organisms were studied. This investigation showed that corn and sorghum field wastes could be effectively used for the production of fuel ethanol thus decreasing the overall amount of green house gases emitted into the atmosphere, dwindling fossil fuel resources and increased gasoline prices.

ICP-65

AGEING STUDY OF PHENOL FORMALDEHYDE RESOL RESIN BY GEL PERMEATION CHROMATOGRAPHY

Rakesh Ranjan, Soumyamol P.B., Korah Bina Catherine and V. Lakshmana Rao

Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre,

Thiruvananthapuram-695022

ABSTRACT

Resol type phenol–formaldehyde (PF) resins, derived from the condensation reaction of phenol with formaldehyde, have been widely used as matrix resin in structural and ablative composites for various space applications.

Despite having wide applications, it has some limitations also. One of the major drawbacks of phenol–formaldehyde resol resin is its low shelf life as the resin is highly temperature sensitive. The shelf life of a polymer can be evaluated using various analytical techniques viz. chromatography, spectroscopy, thermal analysis etc. In the present work, attempts were made to understand the effect of storage temperature on the molecular weight build up of resin by gel permeation chromatography (GPC) which is a widely used polymer characterization method where molecules in solution are separated based on their size. This ageing study of PF resin was carried out over a period of three months.

Resol resin with formaldehyde to phenol ratio (F/P) of 1:1 used as carbon precursor for making ablative silica phenolic composites for space application was chosen for the present study. The resin was stored at three different temperatures i.e. 5°C, 20°C and in ambient condition and analyzed periodically using Waters Alliance 2690 Gel Permeation Chromatograph equipped with differential refractive index detector. Two Styragel columns with a combined separation range of 100 to 20000 D were used. Tetrahydrofuran (THF) with a flow rate of 1ml/min was used as mobile phase. The system was calibrated with polystyrene standard of polydispersity index (PDI) less than 1.2. Third order calibration curve with correlation coefficient 0.9999 were used to calculate the molecular weight. Molecular weight fraction

and free phenol content of the resin was evaluated. A typical GPC curve of PF resin is given in figure 1. A sharp peak was obtained at the extreme right end of the chromatogram, indicating the presence of free phenol content in the resin. Region content is calculated as (i) high molecular weight fraction (greater than 950 D) (ii) middle molecular weight fraction (less than 950 D) and (iii) free phenol fraction.

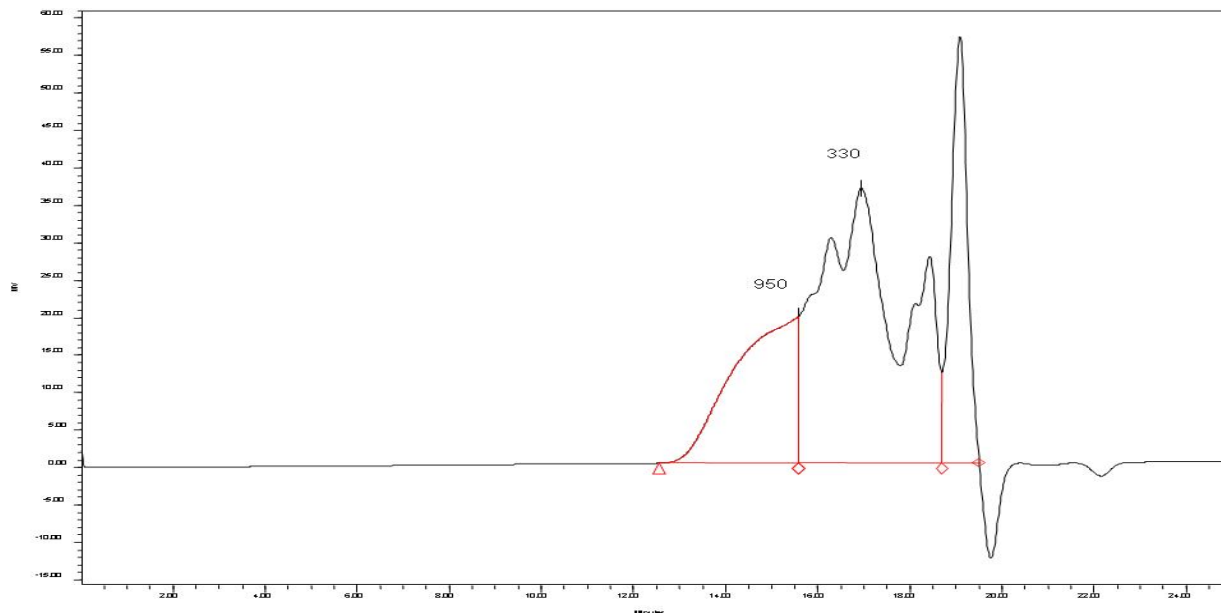


Figure 1: Typical chromatogram of phenol formaldehyde

In case of resin stored at 5°C, there is almost no change within a week in the fractional value for the resin and nominal changes after a month. In case of resin stored at 20°C, free phenol fraction and middle molecular weight fraction decreases while high molecular weight fraction increases with the time. This is due to the combination of low molecular weight fraction with free phenol resulting in the formation of molecule with higher molecular weight. In case of resin stored under ambient condition, the decrease in free phenol and middle molecular weight fraction and increase in high molecular weight fraction is still higher as compared to the resin stored at 20°C.

GPC results revealed that the above changes in the molecular weight fraction are more for higher storage temperature and hence the maximum storage temperature for longer shelf life can be evaluated.

OXIDATION OF BENZENE TO PHENOL BY CERIA-ZIRCONIA AS HETEROGENEOUS CATALYST

Cimi.A.Daniel, S.Sugunan*

Department of Applied Chemistry, Cochin University of Science and Technology

Cochin-682022, Kerala, India.

cimidaniel@yahoo.com, ssg@cusat.ac.in*

Abstract

Ceria-based (CeO_2) catalysts have been extensively investigated because of their major role in three-way catalysis (TWC) for automotive exhaust-gas purification. One of the most important advantages of ceria and zirconia together is their capacity to present a higher oxygen storage capacity.¹⁻² Also, the presence of zirconia stabilizes ceria crystallites, preventing their sintering, especially under severe aging conditions at high temperature.⁴ Ceria-Zirconia has been synthesized using surfactant assisted route. The prepared samples have been characterized by XRD analysis, FT-IR spectroscopic analysis, Thermo gravimetric analysis, Scanning Electron Microscopy (SEM) etc. Ceria-Zirconia has been synthesized using surfactant assisted route. The prepared samples have been characterized by XRD analysis, FT-IR spectroscopic analysis, Thermo gravimetric analysis, Scanning Electron Microscopy (SEM) etc. The activity of the catalyst has been estimated for the direct oxidation of benzene to phenol.

References

- [1] Putna, E. S.; Bunluesin, T.; Fan, X. L.; Gorte, R. J.; Vohs, J. M.; Lakis, R. E.; Egami, T. Ceria Films on Zirconia Substrates Models for Understanding Oxygen-Storage Properties. *Catal. Today*, **50**, 343 (1999).
- [2] Yao, M. H.; Baird, R. J.; Kunz, F. W.; Hoost, T. E. An XRD and TEM Investigation of the Structure of Alumina-Supported Ceria-Zirconia. *J. Catal.*, **166**, 67 (1997).
- [4] Balducci, G.; Fornasiero, P.; Di Monte, R.; Kaspar, J.; Meriani, S.; Graziani, M. An Unusual Promotion of the Redox Behaviour of CeO_2 ZrO_2 Solid Solutions upon Sintering at High Temperatures. *Catal. Lett.*, **33**, 193 (1995).

ICP-67

COMPARITIVE CATALYTIC EFFICIENCY BETWEEN ADSORBED AND COVALENTLY BOUND GLUCOAMYLASE ON MESOPOROUS SILICA

Reni George, S. Sugunan^{*}

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-682022, Kerala, India. Tel: + 91-484-2575804. Fax: +91-484-2577595, Email: ssg@cusat.ac.in, renivgeorge@gmail.com

Abstract:-

Mesoporous silica was synthesized by hydrothermal procedure using tetraethylorthosilicate (TEOS), amphiphilic block co-polymers Pluronic P123 and n-decane as auxiliary chemical under acidic conditions [1]. The amino groups have been grafted to as-synthesized mesoporous silica by 3-aminopropyl trimethoxysilane (3-APTS) [2]. The physicochemical properties of these prepared materials were characterized by Small angle XRD, Nitrogen adsorption – desorption, FTIR, TG/DTG, and SEM experiments. Comparison between adsorbed and covalently bound glucoamylase on mesoporous silica has been studied. Covalently immobilized glucoamylase shows higher catalytic efficiency than adsorbed glucoamylase. . It is clear that surface morphology is very important on the immobilization of enzyme.

References:-

[1] Suman.K.Jana, Reiichi Nishida, Micropor. Mesopor. Mater., **68**,133-142 (2004)

[2] Priti H. Pandya, Raksh V. Jasra, Micropor. Mesopor. Mater., **77**, 67-

77(2005)

ICP-68

A STUDY OF PHYSICO-CHEMICAL PARAMETERS OF GROUND WATER AT ELOOR IN ERNAKULUM DISTRICT OF KERALA, INDIA

A.G. UMADEVI^{*}, M.GEORGE^{*}, JOSE.P.ABRAHAM[§], M.RAJAGOPALAN[§],

DHANYA BALAKRISHNAN[§]

^{*}Department of Chemistry and Research Centre,

Sacred Heart College, Thevara, Kochi-13, Kerala, India

⁵Centre for Environmental & Radiological Sciences,
Department of Physics, The Cochin College, Kochi-2, Kerala, India.

umadeviag@rediffmail.com.

ABSTRACT

The investigation was carried out to study the physico-chemical characteristic of ground water in the Eloor Island, the major industrial belt in Kerala. The major industries in Eloor include phosphate fertilizer plant, monazite industry, caustic soda unit, pesticide plant, aluminum and zinc smelter and factory for synthetic rutile. This localized industrialization warrant an assessment of ground water quality and related environmental aspects. For the present investigation study area was divided into four zones namely East, West, North and South focusing the major industrial spot as the central point and a total of 40 water samples from different locations were collected and analysis has been carried out among the measured parameters using standard methods[1].

The pH of water samples ranged from 3.5 to 7.6 with low values for samples from east and south region. About 42 % of the water samples have pH lower than the BIS prescribed limit of 6.5-8.5. Electrical Conductivity (EC) varies between 101 to 1085 μ mho/cm and total Dissolved Solids (TDS) ranges from 32 to 802 mg/L. About 29 % of samples exceed the desirable limit of 300 mg/L for TDS but lies within the maximum permissible limit prescribed by BIS. Alkalinity was observed in the range 22mg/L to 193 mg/L, within the permissible limit of 200 mg/L.

Total Hardness ranges from 35 mg/L to 402 mg/L showing high values for the samples from west region. The concentration of calcium ranges from 2.1 to 80 mg/L and magnesium ranges from 2.2 - 48 mg/L with slight variation in different locations and in some of the samples (west) it exceeds the desirable limit of 30 mg/L prescribed by BIS but lies within the maximum permissible limit of 75 mg/L. The concentration of potassium ranges from 1 mg/L to 181 mg/L, high concentration of potassium may be due to the influence of the fertilizer plant located in the study area. The concentration of sodium ranges from 1.1 to 33 mg/L, with maximum value in the western region probably due to saline water intrusion. The chloride content ranges from 27 to 992 mg/L, with high concentration for samples in the western region indicating industrial sewage pollution as well as ingress of saline water from backwaters and causes salt taste. A few samples in the northern region exceeds the desirable limit of 250 mg/L prescribed by BIS, but lies within the maximum permissible limit of 1000 mg/L. The concentration of sulphate ranged between 3.5 and 82 mg and nitrate ranges between 4.9 and 42 mg/L indicates there may be possibility for leaching of nitrate to nearby groundwater sources

Significant linear relationship was observed between pH, electrical conductivity, alkalinity, hardness, Ca^{2+} , Mg^{2+} and chloride. From the present study it may be concluded only very few samples showed values above the desirable limits whereas the concentration of parameters in most of the samples are below the limit prescribed by BIS [2].

Reference

1. APHA, Standard methods for the examination of water and waste water. 21st Edn. American Public Health Association, Washinton, D.C, 2000.
2. BIS, Indian standards specifications for drinking water. IS: 10500, Bureau of Indian Standards, New Delhi, 2003.

ICP-69

AUTOMATION OF POTENTIOMETRIC TITRATION FOR THE DETERMINATION OF URANIUM IN NUCLEAR FUEL MATERIALS

Anoop Kelkar, Ashish Pandey, Y.S. Kapoor, Manish Kumar, Mamta Singh, Ajeet Fulzele,

Amrit Prakash, Mohd. Afzal and J.P. Panakkal

Advanced Fuel Fabrication Facility, BARC, Tarapur-401502

anoopkelkar@barctara.gov.in

Advanced Fuel Fabrication Facility is fabricating various types of mixed oxide fuels, namely for PHWR, BWR, FBTR and PFBR. Precise determination of uranium in MOX fuel sample is important to get desired burn up in the reactor. The modified Davies and Gray method [1] is routinely used for the potentiometric titration of uranium. Uranium sample is present as U(VI) in nitric acid solution. Any oxidizing excess of nitrous acid which is left with nitric acid is destroyed by sulphamic acid. Aliquot is brought to 10.5M phosphoric acid medium by addition of conc. H_3PO_4 and U(VI) is reduced to U(IV) using excess of iron (II). The excess of iron (II) is then eliminated using the ammonium molybdate as catalyst by nitric acid. Subsequently U(IV) is titrated to U(VI) using standard $K_2Cr_2O_7$ in a sulfuric acid medium containing vanadyl sulfate to sharpen the end point. Thus the method is cumbersome due to addition of five numbers of reactants to be added at a specific time interval before the titration is started. In order to reduce the manual work and to improve the precision and accuracy automated titrated system have been designed enabling large number of samples to be titrated automatically. For Addition of reagents prior to the titration proceeds via microprocessor controlled piston burettes as shown in figure1. The dosing accuracy and reproducibility of these burettes were $\pm 0.1\%$ and 0.05% respectively. The endpoint of potentiometric titrations were determined by using combined platinum-Silver silver chloride electrode. Titrations were carried out using the potentiometric titrator with an integrated 10 ml burette and a pH meter. It allowed an automatic determination of the inflection point of the titration curve. The titrator is equipped with a microprocessor chip, which controls the complete titration including the volume increment of titrant delivered by the burette.

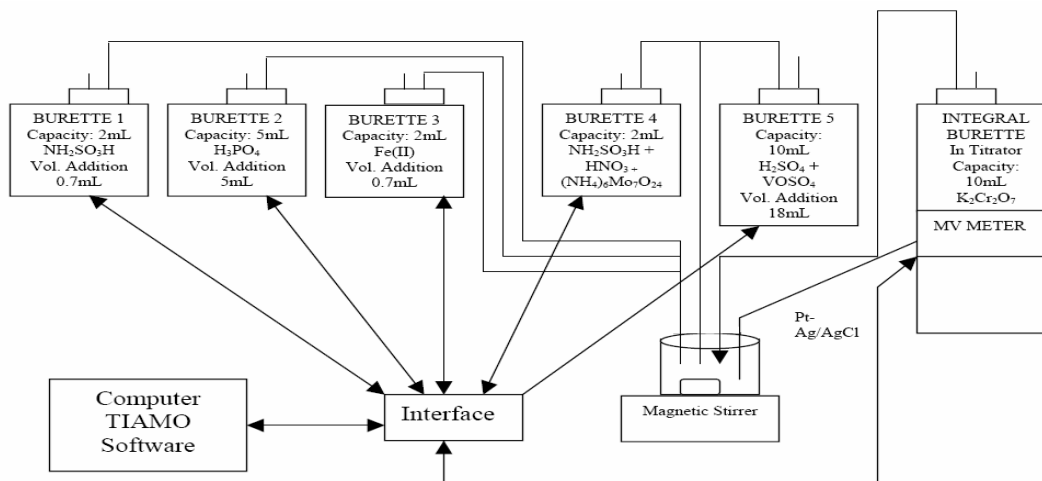


Figure 1. Block Scheme of potentiometric titration set-up

About 95% of $K_2Cr_2O_7$ added initially giving 15 sec for through mixing followed by smaller (0.01mL) and slower addition of $K_2Cr_2O_7$. After each addition, the first derivative of the curve is calculated automatically. Further addition of reagents is stopped after the inflection point of the curve. Arrangements for the analysis of radioactive samples were made in such a way that except titration vessel and magnetic stirrer the burettes and potentiometric autotitrator could be placed out side the fume hood. The different reagents and electrode cable passed through teflon sheet attached at the side wall of fume hood. An interface interconnected the titrator with burettes and computer. It enabled each burette to be addressed individually by the computer for settings in volume and waiting times. The burette's reproducibility at 10ml and its linearity at 6.5ml were checked measuring the mass of water delivered at 23°C. The RSD at 10 ml was 0.1% for 20 determinations. The verification of the delivered volume was made in a similar manner but in steps of 0.5ml. The deviation of the delivered volume compared to the displayed one is given in figure 2. Figure 3 shows typical titration curve for uranium titration. Corrections for the delivered volumes were applied in function of their verifications. Uranium was determined in UO_2 and $(Th,U)O_2$ samples by using auto- titration method.

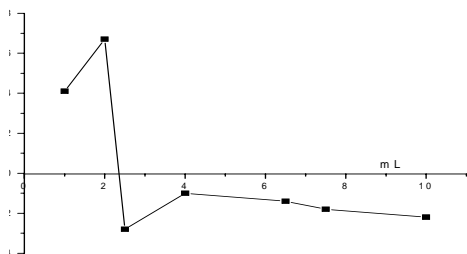


Fig.2 Verification of the 10ml burette
with water at 23⁰C

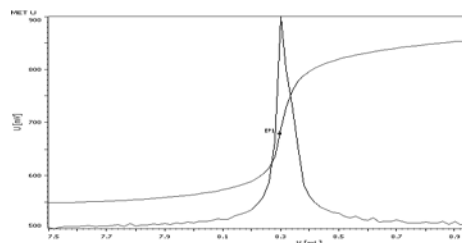


Fig.3 Typical titration curve of U
determination

Effect of sample size on the precision of the U determination was studied. Effect of sample size on the precision of U determination was studied in the range of 1mg to 10mg. The rsd was 0.04% for 11 measurements at 9 mg level when 0.01meq gm⁻¹ K₂Cr₂O₇ was used as titrant. Uranium samples with lower concentration were also determined by using 0.001meq gm⁻¹ K₂Cr₂O₇. Uranium up to 0.2mg could be determined with 0.1% rsd with this method. The lower detection limit for uranium will be very useful in deciding the lower sample size of (Th, ²³³U)O₂ MOX samples.

References:

[1]A.R. Eberle, Lerner, M.Goldbeck and C.Rodden, NBL Report 252 (1970).

ICP-70

DETERMINATION OF ZIRCONIUM BY FLUORIDE ION SELECTIVE ELECTRODE

B.N.Mahanty, V.R.Sonar, R. Gaikwad, S. Raul, D.K.Das, A.Prakash, Md.Afzal and
J.P.Panakkal

Advanced Fuel Fabrication Facility, B.A.R.C., Tarapur-401502

bnmahanty@barctara.gov.in

Zirconium is used in a wide range of applications including nuclear clad, catalytic converters, surgical appliances, metallurgical furnaces, superconductors, ceramics, lamp filaments, anti corrosive alloys and photographic purposes [1]. Irradiation testing of U-Zr and U-Pu-Zr fuel pins has also demonstrated their feasibility as fuel in liquid metal reactors [2]. Different methods that are employed for the determination of zirconium are spectrophotometry, potentiometry, neutron activation analysis and mass spectrometry. Ion-selective electrode (ISE), selective to zirconium ion has been studied for the direct potentiometric measurements of zirconium ions in various samples [3]. In the present work, an indirect method has been

employed for the determination of zirconium in zirconium nitrate sample using fluoride ion selective electrode. This method is based on the addition of known excess amount of fluoride ion to react with the zirconium ion to produce zirconium tetra fluoride at about pH 2-3, followed by determination of residual fluoride ion by fluoride ion selective electrode. The residual fluoride ion concentrations were determined from the electrode potential data using calibration plot. Subsequently, zirconium ion concentrations were determined from the concentration of consumed fluoride ions. A precision of about 2% (RSD) with the mean recovery of more than 94% has been achieved for the determination of zirconium at the concentration of 4.40×10^{-3} moles lit^{-1} . Table-1 contains the data on the determination of zirconium in aqueous solutions.

Table-1: Data on the determination of Zirconium in aqueous solutions by ISE

Zr added (M)	EMF measured (mV)	Free F ⁻ Concentration (M)	Consumed F ⁻ Concentration (M)	Zr obtained (M)	Percentage Recovery
4.40×10^{-3}	87.5	1.55×10^{-2}	1.65×10^{-2}	4.13×10^{-3}	93.9
	87.2	1.57×10^{-2}	1.63×10^{-2}	4.08×10^{-3}	92.7
	87.6	1.55×10^{-2}	1.65×10^{-2}	4.13×10^{-3}	93.9
	87.4	1.56×10^{-2}	1.64×10^{-2}	4.10×10^{-3}	93.2
	88.5	1.49×10^{-2}	1.71×10^{-2}	4.28×10^{-3}	97.3

References:

- [1] N.N. Green wood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984, p. 1113.
- [3] M.B. Gholivand, A. Babakhanian, M. Joshaghani, Zirconium ion selective electrode based on bis(diphenylphosphino) ferrocene incorporated in a poly(vinyl-chloride) matrix , Analytica Chimica Acta 584 (2007) 302–307

ICP-71

DIRECT DENITRATION AND RECYCLING OF PFBR MOX LIQUID WASTE FROM DISSOLUTION TEST USING MICROWAVE HEATING METHOD

R.K.Malay, A.P.Karande, A.K.Fulzele, Y.S.Kapoor, Manish Kumar, Amrit Prakash, Md.Afzal and J.P.Panakkal

Advanced Fuel Fabrication Facility, Bhabha Atomic Research Centre, Tarapur 401 502.

rkmalay@barctara.gov.in

Dissolution test (DT) is one of the important specifications of PFBR MOX fuel. It is a macro homogeneity test used to ascertain that the dissolution of spent fuel will be easier during reprocessing. The DT specification limit for PFBR MOX fuel is ≤ 1.0 wt.% residue of the whole pellet when it is dissolved in HNO_3 under reflux conditions^[1]. For this test, sintered MOX pellet is dissolved in reflux condition in 60 ml of 12M HNO_3 for 10 hours. This test is carried out for each batch and during complete MOX campaign a lot of MOX waste in liquid form is being generated. This liquid waste is in clean form and U and Pu is required to be recovered from the clean waste. Different methods like direct denitration, precipitation and solvent extraction are available but either the product is not of good quality for pelletization or secondary liquid wastes are generated. Microwave denitration is a faster and cleaner method which has different heat transfer mechanism and temperature profile as compared to thermal denitration^[2]. Heat is not transferred from the surface of the container to the core of the feed rather, produced homogeneously within the feed volumetrically and transferred from core to the surface of the container.

An indigenous microwave heating system was fabricated, assembled and modified for glove box adaptation^[3]. It is routinely used for faster dissolution of ceramic materials like UO_2 , $(\text{U,Pu})\text{O}_2$, ThO_2 etc. in our plant. Apart from dissolution, microwave heating can also be used for heating solid materials which are microwave active like UO_2 , $\text{UO}_2(\text{NO}_3)_2$, U_3O_8 and $\text{Th}(\text{NO}_3)_4$. The clean DT liquid waste having $\sim 5\text{g/L}$ of Pu was taken in a 1000 ml capacity quartz beaker and heated in microwave oven with different power program to obtain orange yellow cake of $[\text{UO}_3, \text{PuO}_2]$ which was further heated until a incandescent black fluffy powder of $(\text{U}_3\text{O}_8, \text{PuO}_2)$ was formed. The total time taken for complete solidification was about 2 hours for 500ml of solution^[2]. The gaseous waste was released to exhaust after condensation and scrubbing with 1M NaOH through HEPA filter. The product was further calcined at 700°C and the powder was characterized. The direct denitration of (U-Pu)/nitrate solution using microwave heating shows that the product is free flowing in nature and can be directly used for powder processing^[4].

References

- [1] Specifications based on ASTM for PFBR, No.C, 1008 – 99.
- [2] G.K.Mallik, A.P.Karande, R.K.Malav, V.K.Bhargava, H.S.Kamath, NUCAR, IGCAR, Kalapakkam, 211-213(1995).
- [3]G.K.Mallik, V.K.Gautam, G.Shivasankaran, P.G.Behere, Anand Mohan, V.K.Bhargava, H.S.Kamath, NUCAR, BARC, Mumbai, 427-428(1999).
- [4]G.K.Mallik, R.K.Malav, J.P.Panakkal, and H.S.Kamath, NUCAR, GNDU, Amritsar, 255-256(2005).

ICP-72

STUDY ON THE EFFECT OF UO₂ COMPOSITION ON DISSOLUTION OF SINTERED (Th-U)O₂ MOX BY MICROWAVE HEATING

G. Singh, R K. Malav, A. K. Fulzele, A Prakash., Md. Afzal and J. P. Panakkal

Advanced Fuel Fabrication Facility

BARC, Tarapur-401502

gitendars@barctara.gov.in

Complete dissolution of sample is a prerequisite for any chemical analysis in liquid form. Dissolution of ThO₂ based mixed oxide sample like (Th-U)O₂, (Th-Pu)O₂ is a challenging job due to single oxidation state of thorium (IV).

The present paper describes a study carried out on effect of UO₂ composition on dissolution of sintered (Th-U)O₂ mixed oxide pellets, in 0.05M HF prepared in 16 M HNO₃ [1] . The experiments were performed in PTFE pressure vessels which could stand up to ~ 250°C and safely operated up to 120 psi in an indigenous 700 watts microwave [2] digestion system.

ThO₂, ThO₂-3.75%UO₂ and ThO₂-5%UO₂ pellets (~6g each) were dissolved in 60 mL of 16M HNO₃ / HF mixtures (0.05M HF in 16 M HNO₃) in PTFE (teflon) made pressure vessels (each experiment triplicate) at a pressure of ~ 120 psi. Samples (two at an instant) were withdrawn after each hour and Th in the solution was determined by EDTA complexometric titration [3] where end point was detected visually. Table 1 shows the results of percent dissolution of Th (mean of three experiments) for the sintered pellet after each interval of time until 100% dissolution. Figure-1 shows the plot for percent dissolution of Th (mean Th %) against time taken for sintered pellets.

Application of microwave heating has been applied for the dissolution of uncrushed sintered ThO₂ and (Th-U)O₂ pellets. It is quite evident from Th% dissolved versus time curves that the dissolution is faster as percentage of UO₂ in (Th-U)O₂ MOX solid solution increases. This is attributed to UO₂ as it can easily absorb microwave energy, leading to high temperature. [4, 5].

Table:1 Results of Th percent dissolved, from sintered ThO₂ and (Th-U)O₂ MOX sintered pellets in 0.05 M HF in 16 M HNO₃ in PTFE pressure vessels at a pressure of ~ 120 Psi in 700 watts microwave oven.

Time in Hrs	ThO ₂ in 0.05M HF		ThO ₂ -3.75% UO ₂ MOX in 0.05M HF		ThO ₂ -5% UO ₂ MOX in 0.05M HF	
	Mean	2SD	Mean	2SD	Mean	2SD
	Th %	2σ	Th %	2σ	Th %	2σ
0	0	0	0	0	0	0
1	42.26	1.56	76.31	1.48	95.06	1.98
2	79.28	1.68	94.83	1.24	99.77	0.16
3	87.63	3.82	99.51	0.24		
4	95.29	0.72				
5	97.43	1.82				
6	98.95	0.36				

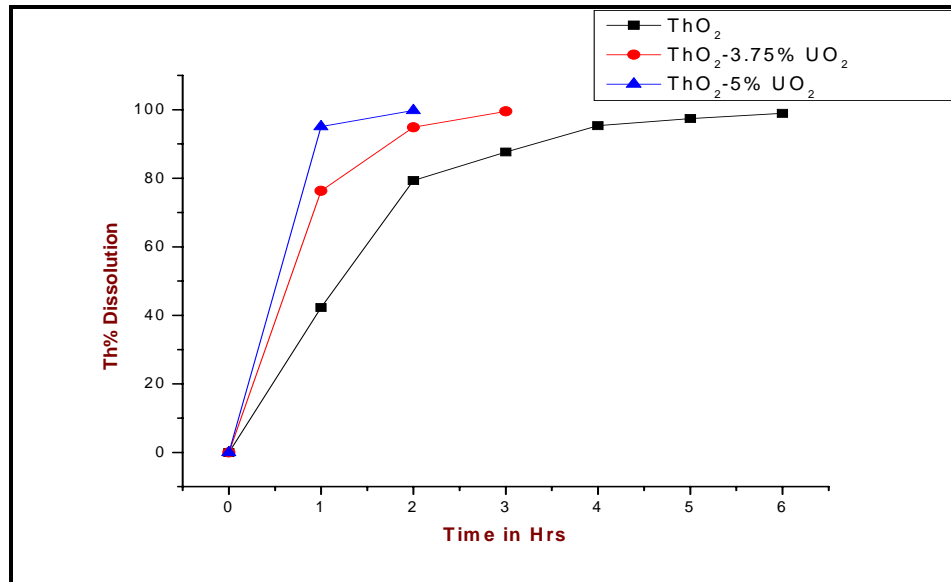


Figure-1: Effect of UO₂ composition on dissolution of Th from sintered (Th-U)O₂ pellets

References:

- [1] W. D. Bond, **ORNL-2519**, Oak Ridge National Laboratory, 1958.
- [2] Y. Jhao and J. Chen, Journal of Nuclear materials, **373** (2008) 53-58.
- [3] A. I. Vogel, Text book of Quantitative Inorganic Analysis, **3rd ed.**, Logmans, Green and Co. Ltd, London, 442.
- [4] C. E. Holcombe, American Ceramic Society Bulletin, **62** (1983) 1388.
- [5] P. A. Hass, American Ceramic Society Bulletin, **58** (1979) 873.

ICP-73

STUDY OF TEMPERATURE PROGRAMMED DECOMPOSITION OF THORIUM NITRATE PENTAHYDRATE

F. A. Khan, K. K. Awasthi, B. N. Mahanty, A. Karande, Amrit Prakash, Md Afzal, J. P. Panakkal

Advanced fuel fabrication facility

BARC, Tarapur
fakhan@barctara.gov.in

Abstract

Thorium based fast reactor nuclear fuel cycle envisages thorax process flow sheet operation at the back end. The product consolidation at this stage would require denitration of thorium solution. Mixed oxides like $(U,Th)O_{2+x}$ can be prepared through co-denitration of respective nitrate salt solution followed by calcinations at high temperature. Various derivatives of $Th(NO_3)_4 \cdot 5H_2O$ are likely to encountered in the denitration as well as calcinations steps. Thermal decomposition of thorium nitrate pentahydrate has been studied in thermo gravimetric analyser (TGA) coupled with evolved gas analyser (EGA) [1]. TGA system has a vertical graphite furnace with PID temperature control and a microbalance of sensitivity 0.04 microgram. High-resolution quadrupole mass spectrometer has been used as a evolved gas analyser. 22.2 mg sample was taken in alumina crucible with the microbalance such that the crucible remained in the middle of the vertical tubular furnace. The sample was heated up to $700^\circ C$ with heating rate $3^\circ C/min$ in the ultra pure argon atmosphere. The flow rate of argon was maintained at 50ml/min. Thermogram and mass spectrum of the sample were simultaneously recorded.

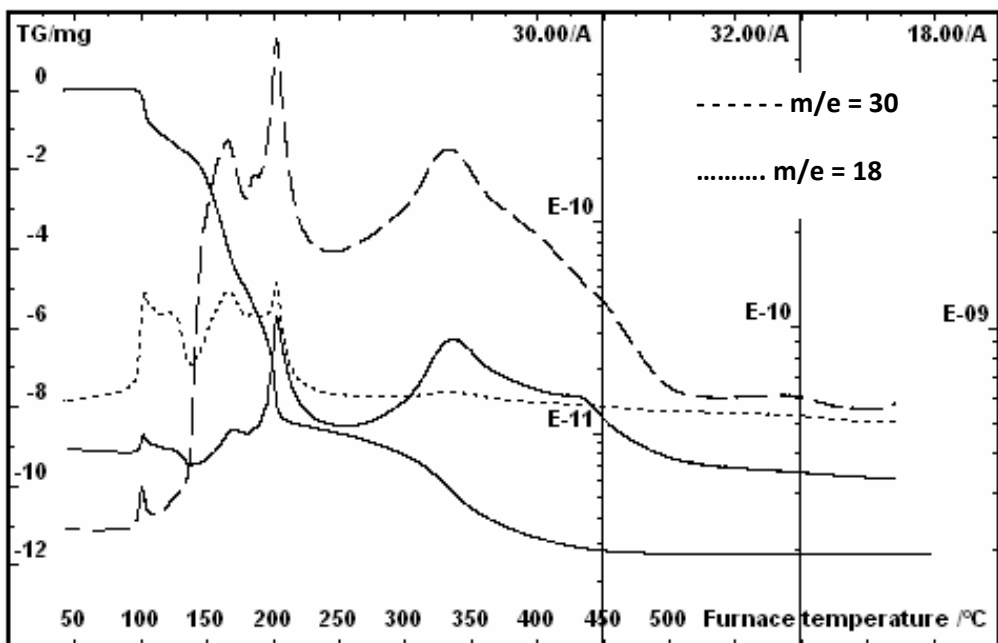


Fig 1: Mass spectrum of Nitric oxide, Water vapour and oxygen evolved from the thorium nitrate pentahydrate superimposed on thermogram of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$

Thermogram of the thorium nitrate pentahydrate showed that the dehydration was started at 97°C and continued up to 212°C . The dehydration of the sample occurred in the three distinct steps, but with the help of mass spectrum of water vapour ($m/e=18$) it could be shown that two more steps might be involved in the dehydration. The mass spectrum of thorium nitrate pentahydrate showed that the evolution of nitric oxide ($m/e=30$) started at 132°C . It indicated that the denitration of the thorium nitrate started well before the completion of its dehydration. Nitric oxide showed three sharp peaks in the mass spectrum of the sample and the position of the peaks was at 166°C , 203°C and 333°C respectively. The mass spectrum of oxygen ($m/e=32$) and nitrogen dioxide ($m/e=46$) followed the mass spectrum of nitric oxide in terms of positioning of peaks on the temperature axis. The current ratio $(m/e=30)/(m/e=32)$ was found to be 5.08, 6.77 and 2.42 respectively and that of $(m/e=30)/(m/e=46)$ was found to be 53.6, 50.0 and 36.6 respectively. The denitration of the thorium nitrate pentahydrate completed at 450°C . TGA-EGA studies indicated a sequential nature of dehydration and denitration phenomena in the temperature range of 40°C to 700°C . Denitration of the thorium nitrate started well before the completion of its dehydration.

References:

[1] S. Dash, M. Kamruddin, P. K. Ajikumar, A. K. Tyagi, Baldev Raj, Santanu Bera, S. V. Narsimhan; Journal of Nuclear Materials **278** (2000) 173-185.

ICP-74

TRACE METAL ASSAY OF THORIUM BASED FUELS BY ICP-AES AFTER MICROWAVE DISSOLUTION.

N.D. Save, S.Ghosh, Rohit Malav, G.Singh, R.K.Jaiswal, Neeraj Kumar, Amrit Prakash, Md.Afzal and J.P. Panakkal

Advanced Fuel Fabrication Facility
Bhabha Atomic Research Centre, Tarapur.

Abstract

Estimation of impurities in nuclear fuel materials like Th/U/Pu is essential prior to their introduction into a reactor[1]. Trace metallic constituents affect the neutron economy, fuel density and fuel fabrication processes. As thorium is an important fuel material for future reactors, its analysis for impurities is also essential. The fuel for AHWR critical facility is (Th,Pu)O₂ and (Th-U)O₂ consisting of approximately 3-4% of PuO₂ and U²³³O₂. However, assay of metallic impurities in such fuel requires quantitative separation of the major matrix from the analytes as Th, U, Pu have rich emission spectrum. ICP-AES is the most suitable technique for trace metal determination because of its simplicity and simultaneous multielement determination capability coupled with adequate sensitivity, analytical range and good precision than other techniques [2]. The present paper describes the analysis of thorium-based fuels for trace metal content after their chemical separation from the major matrix. As thorium has only one oxidation state (IV), its dissolution under normal conditions is very difficult and time consuming. Therefore, a new method under microwave was used [3] for dissolution. Few samples of AHWR type fuel consisting of Thorium and 2.5%UO₂ were dissolved by microwave dissolution technique and analysed for trace impurities by ICP-AES. The results obtained were validated by analyzing ILCE Thoria samples, which have also undergone same process of dissolution and separation.

References:

- [1] A.A.Argekar et al/Talanta **56**(2002)591-601.
- [2] T.K.Sheshagiri et al/Talanta **31**(1984)773-776.
- [3] G.K.Mallik et al/NUCAR (1992)155.

ICP-75

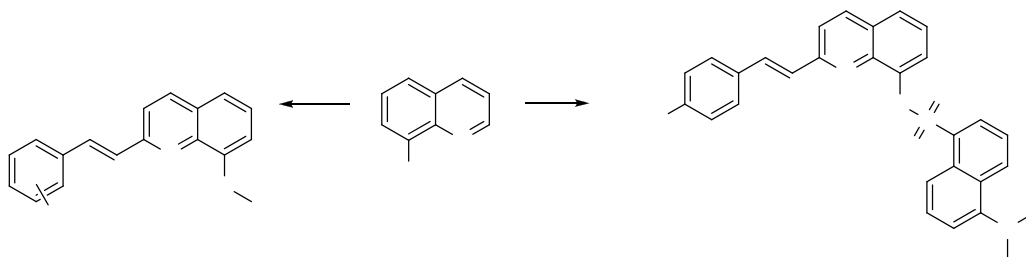
MOLECULAR FLUORESCENT PROBES BASED ON 8-HYDROXYQUINOLINE: EFFECT OF ELECTRON DEFICIENT GROUPS ON CATION SELECTIVITY.

L. Praveen, M. L. P. Reddy* & R. Luxmi Varma*

Chemical Sciences & Technology Division

Abstract

Highly selective cation sensing is imperative for many areas of technology, including environmental, biological, clinical, and waste management applications. For heavy and transition metal ions (e.g., Hg^{2+} , Zn^{2+} , Cu^{2+} and Fe^{2+}), selective sensory protocols are particularly critical due to their high toxicity and crucial role in biological systems. Due to the high sensitivity of fluorescence spectroscopy, allowing the detection of very low concentrations of the analyte, fluorescent sensors and probes have been widely employed¹. 8-Hydroxyquinoline and its derivatives have found many applications in the fluorescent sensing of biological and environmentally important metal ions². Results from our group³ and elsewhere⁴ have shown hydroxyquinoline to be excellent substrates for the construction of fluorescent cation sensors with exceptional selectivity. Recently we have reported thiacalix[4]arene derivative in a 1,3-alternate conformation bearing four quinolinoloxo groups through propyl chains as an excellent chemosensor for Hg^{2+} ions. From our studies, we found that substitution of electron deficient groups and dansyl moiety alters cation selectivity and cation binding mechanisms. The details of the work will be presented.



References:

1. A. P. de Silva, H. Q. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C.P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, 97, 1515.
2. M.A. Palacios, Z. Wang, V. A. Montes, G. V. Zyryanov, Anzenbacher, Jr., *P. J. Am. Chem. Soc.* **2008**, 130, 10307.
3. L. Praveen, V. B. Ganga, R. Thirumalai, T. Sreeja, M. L. P. Reddy, R. Luxmi Varma, *Inorg. Chem.* **2007**, 46, 6277.

4. H. Zhang, L- F. Han, K. A. Zachariaasse, Y-B. Jiang, *Org. Lett.* **2005**, 7, 4217.

ICP-76

VISIBLE LIGHT INDUCED PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE USING SOME TiO₂-POLYANILINE COMPOSITES.

Sandhya K.P., Suja Haridas, S.Sugunan*

Department of Applied Chemistry, Cochin University of Science and Technology

Cochin-682022, Kerala, India.

sandhyakp30@gmail.com, ssg@cusat.ac.in*

Abstract

Photocatalytic degradation is an efficient and economical method to decompose organic pollutants into less dangerous matter. TiO₂ based nano materials have attracted growing attention because they can be used as photocatalyst for effective treatment of wastewater polluted with toxic organic compounds. The dye stuffs from textile and photographic industries are major sources of environmental pollution. The photo degradation of these dye stuffs is important with regard to the purification of dye effluents.

A series of polyaniline-anatase TiO₂ (PANI-TiO₂, Clay-TiO₂-PANI) nanocomposites with different PANI concentrations were prepared. Method involves oxidative polymerization of aniline hydrochloride using Ammonium peroxodisulphate (APS) as oxidant in the presence of anatase TiO₂ cooled in an ice bath via ultrasonication followed by hydrothermal treatment. Catalysts were characterized by XRD, UV-DRS, FTIR, TG analysis, Surface area measurement etc. As the amount of PANI content in the composite decreases the percentage of methylene blue degradation increases. About 93% of MB degradation was obtained within 1 hr using 0.01 g of the catalyst. Clay composites showed lower activity compared to titania polyaniline composites.

ICP-77

**ANALYSIS OF LIQUID-BASED DIETARY SUPPLEMENTS FOR ARSENIC, CADMIUM,
MERCURY AND LEAD THROUGH
UV PHOTOLYSIS AND
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)**

M. V. Balarama Krishna and D. Karunasagar

National Center for Compositional Characterization of Materials (CCCM)
Bhabha Atomic Research Centre
Department of Atomic Energy, Hyderabad – 500 062, India

Email: mvbalaramakrishna@rediffmail.com

Abstract

The consumption of dietary supplements has been on the upsurge over the last two decades because of their perceived beneficial health and medicinal properties [1]. Although organic components having medicinal properties often form the majority of the supplement, dietary supplements also could contain significant quantities of metals due to their ubiquitous nature [2]. Heavy metals are of primary concern due to their toxicity and potential to be present as contaminants or ingredients in dietary supplements. Hence, the demand for rapid, simple and efficient analytical methods to determine heavy element content in different dietary supplements to evaluate essentiality/or toxicity of metals is also continuously increasing.

To meet these objectives, the application of UV-photolysis digestion method using a mixture of HNO₃ and H₂O₂ has been developed for the determination of heavy elements (As, Cd, Pb and Hg) in a variety of liquid-based dietary supplements (ethanolic extracts, liquid-phytocaps and syrups) as a possible alternative to conventional digestion methods. Inductively coupled plasma mass spectrometry (ICP-MS) was used for the quantification of the analytes. Parameters affecting the digestion method such as acid concentration, amount of H₂O₂, digestion time and sample weight were optimized to get the quantitative recovery (>95%) of elements. Total digestion of the sample (i.e. complete colorless solution) can be achieved within 20-40 min by UV irradiation (~300 mg). The clear sample solution thus obtained, was used for analysis. An overall precision of better than 10% could be achieved for many elements. A previously reported closed-microwave digestion method was used for validation. These studies indicate that the UV photo digestion method reported herein is a fast (20-40 min including pre-digestion time) and simple method for the determination of the selected toxic metals.

References:

1. World Health Organization (WHO) guidelines for assessing quality of herbal medicines with reference to contaminants and residues, World Health Organization, Geneva (2007).
2. S. G. Capar, W. R. Mindak, J. Cheng, Analysis of food for toxic metals, Anal. Bioanal. Chem., 389, 159 (2007).

ICP-78

**INFLUENCE OF OF NANO METAL OXIDES ON THERMAL
DECOMPOSITION OF AMMONIUM PERCHLORATE SOLID
PROPELLANT OXIDISER OF VARYING PARTICLE SIZES**

Soumyamol P.B., S. Saranya*, Salu Jacob, R. Rajeev, Korah Bina Catherine, V.L. Rao

Analytical and Spectroscopy Division, PSCG/PCM, VSSC, Trivandrum – 695 022

*M.Sc. Student, University of Kerala

e-mail : k_binacatherine@vssc.gov.in

Abstract

The oxidizer in a composite solid propellant accounts for around 70% by weight of the propellant and hence has major influence on propellant properties. Commonly used oxidizers are ammonium perchlorate (AP), potassium perchlorate, ammonium and potassium nitrates, etc. Owing to desirable characteristics like high density, high thermal stability, low hygroscopicity, compatibility with other propellant ingredients, good performance and availability, AP dominates the solid propellant oxidizer field [1]. The particle size of AP is a critical factor influencing the burn rate properties of the propellant. A burn rate catalyst plays a dual role of accelerating the decomposition of AP and promoting the oxidation of the fuel [2]. The number of active sites, surface area and particle size control the catalytic activity. Examples of burn rate modifiers are copper chromite, copper oxide, ferric oxide, etc. Nano materials with high surface area show excellent catalytic activities [3] and nano transition metal oxides are finding increasing application as burn rate modifiers.

In this work the thermal decomposition behaviour of AP of three different particle sizes, viz., coarse (320 μm), fine (45 μm) and ultra fine (4.5 – 5.8 μm) manufactured in VSSC was studied using thermogravimetry (TG). Nano oxides of transition metals copper, manganese and iron were prepared in the laboratory by an inorganic condensation method from their corresponding chlorides using a PEG surfactant template [4,5] and their effect on the thermal decomposition of AP in

inert atmosphere at a heating rate of 10°C/min was investigated using platinum crucibles.

Results and Discussion

Effect of particle size of AP on thermal decomposition

AP is reported to decompose in two stages, both exothermic in nature with a mass loss of approximately 30% for the low temperature decomposition (LTD) and 70% for the high temperature decomposition (HTD). However, the decomposition patterns of AP of different particle sizes showed major differences with respect to mass loss in LTD and HTD, but the decomposition temperature range was reduced in the case of ultra fine AP only.

The influence of particle size on the decomposition pattern can be explained as follows : ammonia (NH₃) gas formed during the decomposition of the first stage covers the surface of the partially decomposed AP powder thereby preventing further decomposition. With increase in surface area of fine and ultra fine AP compared to coarse AP, the rate of first stage decomposition is high, producing larger quantities of NH₃ during the low temperature decomposition. This NH₃ gas effectively covers the surface of AP crystals hindering further decomposition at low temperature. This will lead to lowering of mass loss during LTD in fine and ultra fine AP. However with increase in temperature, the NH₃ gas starts to desorb from the surface of AP and 2nd stage decomposition begins.

Effect of nano transition metal oxides on thermal decomposition

All the three transition metal oxides employed in the study catalysed the thermal decomposition of AP with respect to temperature and mass losses, although the extent varied with particle size of AP. With coarse AP, the temperature interval of decomposition reduced from 152°C to 112, 134 and 137°C with oxides of Cu, Mn and Fe respectively. In the case of fine AP the corresponding values reduced from 150°C to 104, 141 and 142°C and with ultra fine AP the values reduced from 133°C to 90, 122 and 144°C respectively. In all three cases, catalytic effect of the oxides was in the order Cu > Mn > Fe. The reduction potential of Cu²⁺/Cu⁺/Cu system is lower than the reduction potential of the other two systems. Hence copper oxide favours the catalytic decomposition of AP more than the other oxides by promoting the electron transfer during the thermal decomposition of AP.

Mass losses of LTD increased in presence of nano copper oxide for coarse AP, while fine AP showed increase both with copper and manganese. Ultra fine AP showed twice the mass loss in LTD in presence of copper oxide only, with no effect in the other two cases.

SURFACE PROPERTIES AND CATALYTIC ACTIVITY OF PURE AND MODIFIED MESOPOROUS SBA15 MATERIALS

AMBILI V. K. AND S. SUGUNAN*

Department of Applied Chemistry, Cochin University of Science and Technology

Cochin-682022, Kerala, India.

ambilivk@yahoo.com, ssg@cusat.ac.in*

ABSTRACT

Application of mesoporous materials in catalysis is very interesting area based on the fact that mesoporous materials can be used as relatively well-described model materials due to their well-defined chemical properties of the surface. Among the mesoporous materials, SBA-15 is regarded as one of the most promising materials because of its higher surface area, large pore size and higher hydrothermal and thermal stability. The ordered mesoporous structure and large pore size of SBA-15 are likely more favorable to the diffusion of reactants and products. Thus heteroatom containing SBA-15 should be regarded as good catalyst candidates for some catalytic reactions. The metal incorporated SBA 15 materials are expected to be useful as a selective catalyst for reactions involving large molecules. In the present work tungsten supported mesoporous SBA-15 molecular sieves have been synthesized under direct synthesis method. Prepared materials were characterized by powder X-ray diffraction (XRD), nitrogen adsorption, UV-vis diffuse reflectance spectroscopy technique, FT-IR, SEM etc. One-pot acetalization of cyclohexanone was carried out using methanol over the prepared catalysts. The results showed that W-SBA15 materials were more catalytically active in acetalization reaction.

References

- 1 A. Vinu, V.Murugesan, W.Bohlmann, M.Hartmann, J.Phys.chemB 108(2004) 11496.
- 2 Chino N, Okubot, Microporous Mesoporous Mater. 87 (2005) 15.
- 3 Gene V E, Altay F E, Uner D, Catal. Today 105 (2005) 537.
- 4 Y. Li, Z. Feng, Y. Lian, K. Sun, L. Zhang, G. Jia, Q. Yang, C. Li, Micropor.Mesopor.Mater. 84 (2005) 41.
- 5 S. C. Laha, P. Mukerjee, S. R. Sainkar, R. Kumar, J. Catal. 207 (2002) 213

ICP-80

**MECHANICAL CHARACTERIZATION OF VARIOUS FIBERS FOR AEROSPACE
APPLICATION USING DIFFERENT METHODS**

Neeraj Naithani*, C. Suchithra, R. Sadhana and V. Lakshmana Rao

Analytical and Spectroscopy Division

Vikram Sarabhai Space Centre, Thiruvananthapuram-695022

Email: neeraj_naithani@vssc.gov.in

Abstract

Composites are the best choice for the new age structural materials for aerospace applications. Fiber reinforced composite have shown good performance in this area. To select better reinforcement, it is required to characterize the reinforcement material prior to use. For that, testing single filament is better choice. To test single fiber conventional method is to get the breaking load using universal testing machine and then measure radius either by mass per unit length or through optical measurement. Another option is fiber testing machine with high resolution load cell and in-built vibroscope to measure linear density. This paper deals with the comparative study of the test method to characterize single fiber using both the methods.

To compare the two methods T-300 carbon fiber, Twaron 1056 and Twaron 2200 were tested using Favimat fiber testing machine and universal testing machine. To get the tensile strength the diameter is calculated from the measured value of mass per unit length (MUL) by considering the fiber as long cylinder. In fiber testing machine linear density of each single fiber was measured using vibroscopic method. Tanacity and linear density obtained from the fiber testing machine is converted into tensile strength and diameter using the mathematical correlation. The result showed lot of scatter in value which is attributed due to irregular shape of single fiber and surface defects occurred during separation of single fiber. To overcome the effect of scattering around 20 single fibers were tested in one batch. The results show that the characterization of fibers using fiber testing machine is better choice as it is fast, hassle free and consume less time without much compromising with the accuracy.

ICP-81

**SYNTHESIS, CHARACTERIZATION AND OPTICAL PROPERTIES OF A HIGH NIR
REFLECTING YELLOW INORGANIC PIGMENT: Mo⁶⁺ DOPED Y₂Ce₂O₇ AS A COOL
COLORANT**

V.S. Vishnu and M.L.P. Reddy*

Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Thiruvananthapuram 695 019, Kerala, India

*Email: mlpreddy55@gmail.com

Abstract

Pigments possessing the ability to confer high solar reflectance have received considerable attention in recent years. The inorganic class of NIR reflective pigments are mainly metal oxides and are primarily employed in two applications: (i) visual camouflage and (ii) reducing heat build up. More than half of the solar radiation consists of near-infrared radiation (52%), the remaining being 43% visible light and 5% ultraviolet radiation [1]. Over heating due to solar radiation negatively affects comfort in the built environment and contributes substantially to electrical consumption for air conditioning and release of green house gases. A pigment which has strong reflections in the NIR region (780–2500 nm) can be referred to as a “cool” pigment. However, most of the NIR reflective inorganic pigments particularly yellow (eg. cadmium yellow, lead chromate, chrome titanate yellow etc.) contain toxic metals and hence their consumption is being limited. Replacing them with environmentally benign cool pigments that absorb less NIR radiation can yield coatings similar in color, but with higher NIR reflectance.

A new class of yellow inorganic pigments possessing high near-infrared reflectance (above 90% at 1100 nm), having the general formula $Y_2Ce_{2-x}Mo_xO_{7+\delta}$ (x ranges from 0 to 0.5) were synthesized by traditional solid state route [2]. The synthesized samples were characterized by powder X-ray diffraction, Scanning Electron Microscopy, UV-Vis-NIR Diffuse Reflectance Spectroscopy, CIE 1976 $L^*a^*b^*$ color scales and TG/DTA analysis. XRD analysis reveals the existence of a major cubic fluorite phase for the pigment samples. The diffuse reflectance analysis of the pigments shows a significant shift in the absorption edge towards higher wavelengths (from 410 nm to 506 nm) for the molybdenum doped samples in comparison with the parent compound. The band gap of the designed pigments changes from 3.01 to 2.44 eV and displays colors varying from ivory white to yellow. The coloring mechanism is attributed to the O_{2p} – Mo_{4d} charge transfer transition. The ability of the pigment to confer its high NIR reflectance on to a roofing material was evaluated by coating the typical pigment $Y_2Ce_{1.5}Mo_{0.5}O_{7+\delta}$ over asbestos cement sheet by a two step process. In the first step, a small strip of asbestos is pre-coated with TiO_2 , an inexpensive white pigment possessing high NIR reflectance. In the second step, the designed typical pigment is applied to the pre-coated substrate material. The yellow pigment over TiO_2 base coat coating exhibited an NIR reflectance of 86.8% at 472 μm thickness. The designed pigments are environmentally benign and effectively confer their NIR reflectance properties to a roofing material like asbestos.

References

- [1] P.Jeevanathan, R.S.Mulukutla, M.Philios, M.Chaudhuri, L.E.Erickson, K.J.Klabunde. J. Phy. Chem. C, **111**, 1912 (2007).

[2] V.S.Vishnu, M.L.P.Reddy. Chem. Lett. **39**, 820 (2010).

ICP-82

THE SYNTHESIS, CHARACTERIZATION AND OPTICAL PROPERTIES OF Si^{4+} AND Pr^{4+} DOPED $\text{Y}_6\text{MOO}_{12}$ COMPOUNDS: ENVIRONMENTALLY BENIGN INORGANIC PIGMENTS WITH HIGH NIR REFLECTANCE

Giabile George and M. L. P. Reddy*

Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Thiruvananthapuram 695 019, Kerala, India

*E-mail address: mlpreddy55@gmail.com

Abstract

Much interest has attended roofing materials with high solar reflectance and high thermal emittance, so that interiors stay cool, thereby reducing the demand for air conditioned buildings [1]. The heat producing region of the infrared radiations ranges from 700–1100 nm. Replacing conventional pigments with “cool pigments” that absorb less NIR radiation can provide coatings similar in color to that of conventional roofing materials, but with higher solar reflectance. NIR reflective pigments have been used in the military, construction, plastics and ink industries. Complex inorganic pigments based on mixed metal oxides (eg., chromium green, cobalt blue, cadmium stannate, lead chromate, cadmium yellow and chrome titanate yellow), which have been used in camouflage, absorb visible light but reflect the NIR portion of incident radiation [2]. However, many of these pigments are toxic and there is a need to develop novel colored, NIR-reflecting inorganic pigments that are less hazardous to the environment.

In this work, a series of NIR reflective colored pigments of formula $\text{Y}_{6-x}\text{M}_x\text{MoO}_{12+\delta}$ (where $\text{M} = \text{Si}^{4+}$ or Pr^{4+} and x ranges from 0 to 1.0) were synthesized by traditional solid-state route and applied to asbestos cement roofing material so as to evaluate their use as ‘cool pigments’ [3]. The phase purity of the calcined pigment samples were determined using powder X-ray diffraction. The diffuse reflectance of the powdered pigment samples were measured using a UV–Vis–NIR Spectrometer. The $L^*a^*b^*$ color coordinates were evaluated by CIE 1976 color scale. Replacing Si^{4+} for Y^{3+} in $\text{Y}_6\text{MoO}_{12}$ changed the color from light-yellow to dark-yellow and the band gap decreased from 2.60 to 2.45 eV due to O_{2p} - Mo_{4d} charge transfer transitions. In contrast, replacing Pr^{4+} for Y^{3+} changed the color from light-yellow to dark brown and the band gap shifted from 2.60 to 1.90 eV. The coloring mechanism is based on the introduction of an additional $4f^1$ electron energy level of Pr^{4+} between the valence and conduction bands. Most importantly, the pigments exhibited high NIR reflectance (75 to 85%) when coated on asbestos cement sheet, thus rendering them excellent candidates for use as ‘Cool Pigments’.

References

- [1] P.Jeevanathan, R.S.Mulukutla, M.Phillips, M.Chaudhuri, L.E.Erickson, K.J.Klabunde. J. Phys. Chem. C 111,1912 (2007).
- [2] R.Levinson, P.Berdahl, H.Akbari. Sol. Energy Mater. Sol. Cells 89,351 (2005).
- [3] Giable George,V.S.Vishnu, M.L.P.Reddy. Dyes Pig. doi:10.1016/j.dyepig.2010.05.010 (in press).

ICP-83

OPTIMIZATION OF SEPERATION AND DETECTION CONDITIONS FOR THE MULTI RESIDUE ANALYSIS OF ORGANOCHLORINES AND ORGANOPHOSPHORUS PESTICIDES BY GC-MS/MS

M.C.Khetagoudar, Mahadev B. Chetti*, Deepa G.T., P.T.Goroji., Dinesh B.K.

*Corresponding author : Dean (Agri.), University of Agricultural Sciences, Dharwad – 580 005, Karnataka, India,
Cell : 094484 95309, Fax : +91-836-2792180, E-mail address : mbchetti_uas@rediffmail.com

ABSTARCT

A comprehensive GC-MS/MS method was optimized for multiresidue analysis of organochlorines and organophosphorus pesticides using Waters triple quadrupole mass spectrometer (qQq) (RAB 120) coupled with Agilent GC (6890) containing DB-5MS (30 M, 0.25 μ id,) capillary column. The method resolved the co-elution problems as observed in full scan GC–MS analysis and allowed chromatographic separation of Ops, OCs pesticides within 25 min run time with NIST library-searchable mass spectrometric confirmation with two MRM mass transitions. Thorough optimization was accomplished for the oven temperature programming, ion source temperature, collision energy, dwell time etc. to achieve best possible separation of the test compounds. The adjustment of all parameters substantially increased the sensitivity of the MS–MS mode. The best results obtained for OCs and OPs will be described.

Keywords: GC-MS/MS ; Pesticide residues; OPs; OCs; Multiresidue analysis; Optimization

ICP-84

QUALITY ASPECT FOR VOD OF SMALL COLUMNS OF EXPLOSIVE CHARGE

¹Biswa Ranjan Mohanty, ¹Joseph Marcelin, ¹Shyam Sundar Manna, ²P.Radhakrishnan Nair

¹Quality Division - Propellants and Chemicals (QDPC), ²Quality Assurance and Reliability Propellants and Chemicals Group (QRP), Vikram Sarabhai Space Centre,

Indian Space Research Organization, Thiruvananthapuram – 695022

Email: brm0307@gmail.com, biswaranjan_mohanty@vssc.gov.in

ABSTRACT

Explosives are now being used in wide scale for a variety of purpose. Only a few percent is being used for research and application purpose like space transport, medical etc. The main criteria for a chemical compound to be an explosive is that it should be in a unstable condition (by its spatial configuration) and on explosion the products should be much stable than the reactants. Normally the fuel is Carbon/Hydrogen, and the oxidizer is Oxygen/Halogen. The striking feature of an explosive is that it is self sustained i.e. the fuel and oxidizers are already present in the explosive. For this reason explosives are often called as condensed explosives. The next striking factor is the speed of reaction. The reaction speed of TNT is in milliseconds hence the rate of production of energy (energy released per second) is much much higher than Coal, Petrol or Kerosene. This speed decides the usefulness of the explosive. Thus the deciding factor of an efficient explosive is: Amount of energy available in the explosive and the rate of release of the available energy when triggered. The various parameters to find this two factors are: Heat of explosion, Temperature and Pressure of explosion, Power index, Rate of burning, Velocity of Detonation (VOD) and Detonation pressure. Most of the explosives contain the elements C, H, N, O. In general the formula is $C_aH_bN_cO_d$. Here the oxygen or simply the Oxygen balance matters for the effectiveness of the explosive: e.g. For nitro glycerin Oxygen balance is +3.5 %, For RDX it is -22% and For TNT it is -74%. If the Oxygen balance = 0, it is referred as the most desirable or ideal condition. Any deviation to the (+) ve or (-) ve side will result in a comparatively lower heat of explosion and thus a lower performance. In space application the quality of the explosive is an important factor. Mainly two indicators are measured for the performance of explosives, they are: Detonation velocity and pressure. Explosive velocity, also known as detonation velocity, is the velocity at which the shock wave front travels through a detonated explosive. Explosive velocities are always faster than the local speed of sound in the material. As we know that the VOD is the only measurable magnitude related to an explosive that can be given a number with certainty, it is easy to comprehend why it has been

overemphasized as an indication of explosive strength. VOD is a function of the explosive configuration, charge diameter and confinement. Charge diameter and confinement are generic environment variables for any given blast. The same explosive in different environments will result in different VODs. Rather than strength, VOD gives an idea of the relative indication of the energy partitioning between shock and heave. The higher the VOD, the higher the shock component in relation to the total energy. While low VOD explosives will shift the energy partition towards a higher proportion of heave. In any case, the VOD should have to be measured with a confinement in order to be meaningful.

If the explosive is confined before detonation then the force produced is focused on a much smaller area, and the pressure is massively intensified. This results in explosive velocity that is higher than if the explosive had been detonated in open air. Unconfined velocities are often approximately 70 to 80 percent of confined velocities. Explosive velocity is increased with smaller particle size, increased charge diameter, and increased confinement. Typical velocities in solid explosives often range beyond 4000 m/s to 10300 m/s. This paper brings out a comparison of VOD measured by various methods.

Experiments data were obtained [1] for detonation of small columns of PETN for finding out the velocity of detonation of explosive.

PETN gives $3\text{CO}_2 + 2\text{CO} + 2\text{N}_2 + 4\text{H}_2\text{O}$

It is obvious that a large positive heat of formation of the explosive favours a high Temperature. Another important property of an energetic material is its density. Based on a number on results it was seen that for a constant length there was no deflagration from a charge density of 0.7gm/cc to 1.45. Further study to be done for studying the deflagration to detonation transition. Here the velocity of detonation of boosters are taken into consideration

VELOCITY OF DETONATION: The detonation velocity in cylindrical charge decreases with decreasing diameter because of radial expansion and loss of energy. When the diameter approaches infinity it is termed as ideal detonation velocity. This decreases with decreasing initial density (ρ) and the velocity reaches maximum when the density equals the crystal density. The equation followed by PETN charge in circular shape given by Friedrich (1933) [2] as:

$$D = 2.8 + 2.8 (\rho)^{1.3} \dots 1$$

Where D is velocity of detonation in Km/Sec.

ρ is the density in gm/cc

The boosters generally used is of around the density of 1.25 gm/cc (approx)

From the above equation we will get

$$D = 2.8 + 2.8 (1.25)^{1.3}$$

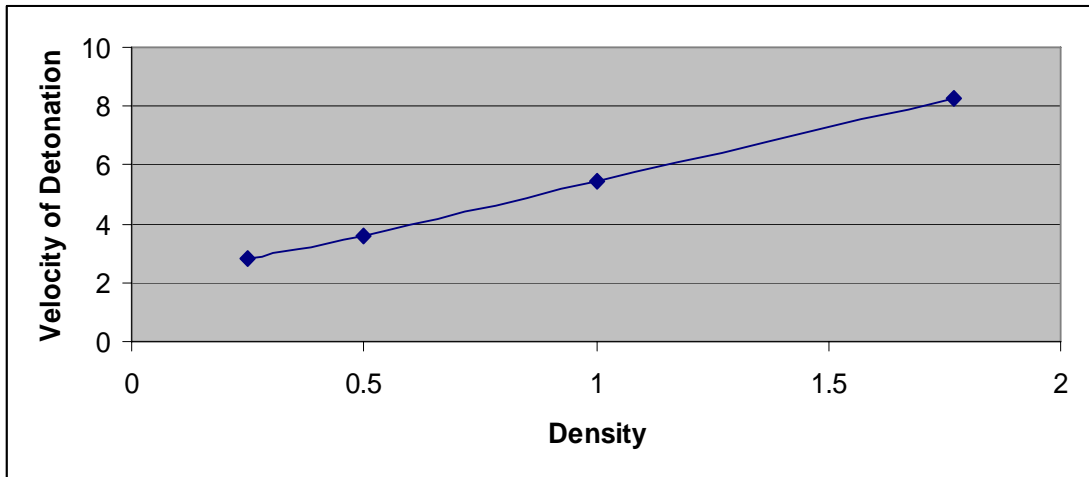
$$D = 6.5 \text{ Km/sec.}$$

So theoretically this velocity is required for a density loading of 1.25gm/cc to have a stable detonation.

The VOD of PETN at various densities are as follows [1]

Density :	0.25	0.50	1.00	1.77
-----------	------	------	------	------

VOD :	2.83	3.60	5.48	8.30
-------	------	------	------	------



Density Vs. Velocity of Detonation

So from the equation of Friedrich we can compare the velocity for the corresponding densities

Density :	0.25	0.50	1.00	1.77
-----------	------	------	------	------

VOD :	3.26	3.94	5.60	8.68
-------	------	------	------	------

With minor variation the results of both methods are nearly same.

References:

1. [1] Mohammad Hossein Keshavarz and Hamid Reza Pouretedal ,Predicting the Detonation Velocity of CHNO Explosives by a Simple Method, Department of Chemistry, Malek-Ashtar University of Technology, Shahin-Shahr
2. [2] Johansson & Persson, Detonics of high explosives (1970)
3. R. A. Strehlow, Combustion Fundamentals, McGraw-Hill, New York, 1985
4. H. C. Hornig, E. L. Lee, M. Finger and J. E. Kurrie, Equation of State of Detonation Products, 5th Symposium (International) on Detonation, Pasadena, CA, August 1970
5. On Some Methods of Determination of the Detonation Energy of Explosives,
W. A. TRZCIŃSKI ,Military University of Technology, Warsaw, PL

ICP-85

DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMETRIC METHOD FOR THE DETERMINATION OF Ni(II) AND Co(II) IN WATER AND VEGETABLE SAMPLES USING ANALYTICAL REAGENT 2,2'-(BENZENE-1,2-DIYLBIS(NITRILOMETHYLIDENE))DIPHENOL

***P. Reddy Prasad and ^{a*}N.Y.Sreedhar**

^{a*}*Electroanalytical Lab, Department of Chemistry, S.V.University, Tirupati-517502, A.P., INDIA.*

^{a*}*Corresponding author. Tel: +91 877 2232656,E-mail address: sreedhar_ny@rediffmail.com*

Abstract

A highly, selective and fairly rapid and economical method for the determination of Ni(II) and Co(II) by differential pulse anodic stripping voltammetric method was developed using 2,2'-(benzene-1,2-diylbis(nitrilomethylidene))diphenol as a complexing reagent onto hanging mercury drop electrode(HMDE). The optimum experimental conditions were found to be 2,2'-(benzene-1,2-diylbis(nitrilomethylidene))diphenol concentration of 3.0mM, NH₃-NH₄Cl buffer (pH-9.0), scan rate of 12mV/sec, accumulation potential of -300 mV versus Ag/AgCl, accumulation time of 180s, and pulse

amplitude of 50mV. The peak currents of Ni(II) and Co(II) were directly proportional to the initial metal concentration in the ranges of 0.01-90µg/mL under the optimized conditions. A relative standard deviation of 0.52%(n=5) was obtained, and the limit of detection was found to be 0.0042 and 0.0026 µg/ml for Ni(II) and Co(II) respectively. The method was applied to the determination of Ni(II) and Co(II) ions in water and vegetable samples with satisfactory results.

Keywords: Differential pulse anodic stripping voltammetry (DPASV), nickel and cobalt.

ICP-86
PREPARATION AND CHARACTERIZATION OF NANOGOLD
SUPPORTED OVER Zr/SBA 15

Soumini C, Sugunan S*

Department of Applied Chemistry,
Cochin University of Science and Technology, Kochi-682 022, India.
Ph: +91 484-2575804. Fax: +91 484 2577595

E-mail: ssg@cusat.ac.in , souminijju@gmail.com

Nanogold catalysis, because of its unique properties has become a well established choice for many chemical transformations with pre-eminence established now in both heterogeneous and homogeneous catalysis [1]. In the present work, nanogold is supported over Zr doped SBA 15 mesoporous silica. Nanogold is prepared using chloroauric acid solution under basic conditions [2]. Zr doping is done over SBA 15 via simple impregnation method using Zirconyl nitrate as the precursor. The prepared systems are characterized using various experimental techniques. Efficient dispersion of small sized nanogold particles are confirmed from the absence of XRD peak around 2θ value of 38°[3]. FTIR spectra indicate the formation of Zr-O-Si bonding. The morphology of SBA 15 remains unaffected even after high percentage loading of Zirconia as well as introduction of nanogold which is evident from SEM photographs.

References:

- [1] A.Corma, Catal. Rev. - Sci. Eng., 2004, 46,369-417.
- [2] T.Ito, J.H. Lunsford, Nature 314 (1985) 721–722.

[3] Nikolay Petkov, Norbert Stock, and Thomas Bein, J. Phys. Chem. B 2005, 109, 10737-10743.

ICP-87

**SYNTHESIS, CHARACTERIZATION AND PHOTO CATALYTIC ACTIVITY OF Ni-TiO₂
FOR THE DEGRADATION OF 2,4-DICHLOROPHRNOXY ACETIC ACID IN THE
VISIBLE REGION**

Mothi Krishnamohan and S. Sugunan*

Department of Applied Chemistry

Cochin University of Science and Technology, Kochi-682 022,.

E-mail: mothikrishnamohan @gmail.com, ssg@cusat.ac.in

Abstract

Titanium dioxide has been widely used to solve environmental problems associated with organic pollutants due to its chemical stability, nontoxicity and high photo catalytic activity^{1,2}. But the wide band gap limits the possibility of employing visible light which is found in solar light^{3,4}. The efficiency of TiO₂ can be enhanced by three methods, namely increasing its surface to volume ratio, sensitization using dye molecules and doping of non metals such as N, C and S and addition of metal ions. The ions reported to be doped in to the lattice of the TiO₂ include Pt, Ag, Au, Cu, Ni and Pd for prevention of electron and holes recombination.⁵ This is due to the reason that a metal with a work function higher than that of the semiconductor provides a Schottky barrier that facilitates the transfer of electrons from the semiconductor to the metal thus improving the catalytic efficiency. In this work we have prepared Ni-TiO₂ by hydrothermal route. The prepared catalyst was characterized by using XRD, IR spectroscopy, UV-DRS, TG, SEM, EDAX and BET surface area measurements. XRD result shows that anatase is the major phase in the prepared sample and no peak corresponding to the metal is formed. This may be due to the low concentration of metal in the Titania system. From the TG results we could understand that the calcination temperature of the prepared sample was 500⁰C. The catalyst was able to absorb light from the visible region, was supported by UV-DRS. Morphology of the sample was determined by using SEM and observed that particles are almost spherical in shape. EDAX analysis was used to understand the percentage of metal ion present in the Titania system. Surface area of the sample was determined using BET measurements. Photo catalytic activity of the sample was studied using the herbicide 2,4-Dichlorophenoxy acetic acid by Uv- spectrophotometer. More than 80% of the sample was degraded within one hour. We have compared the efficiency of the catalyst with pure Titania prepared by same method and also the Aldrich Titania. The Ni-TiO₂ has got maximum activity compared to Pure Titania and Aldrich Titania. This may be due to the better charge separation in the prepared catalyst⁶.

References:

- 1) M.R. Hoffmann, S.T. Martin and W.Choi, Environmental applications of semiconductor photocatalysis, *Chem.Rev.*, **1995,95, 69-96.**
- 2) P.Pichat, *Chemical Degradation methods for Wastes and Pollutants: Environmental and Industrial Applications*, ed. M.A.Tarr, Marcel Dekker, Inc., New York, Basel, **2003, pp.77-119.**
- 3) S.Sato, Photocatalytic activity of NO_x-doped TiO₂ in the visible light region, *Chem.Phys.Lett.*, **1986, 123, 126-128.**
- 4) J.C, L. Wu and J.Lin, Microemulsion mediated solvothermal synthesis of nanosized CdS sensitized TiO₂ crystalline photocatalyst, *Chem.Commun.*, **2003,1552-1553.**
- 5) Fuerte,A., Hernandez-Alonso, M.D.,Maria, A.J.,Martinez-Arias, A., Fernandez-Garcia, M.,Conesa, J.C.,Soria, J.Visible light activated nanosized doped-TiO₂ photo catalysts. *Chem. Commun.* **2001, 2718-2719.**
- 6) Rajesh J.Tayade, Ramachandra G.Kulkarni and Raksh.V.JAsra, *Ind.Eng.Chem.Res.***2006, 45, 5231-5238.**

ICP-88

CHELATION ION CHROMATOGRAPHY ON 1-(2-PYRIDYLAZO)-2-NAPHTHOL LOADED TITANIUM PHOSPHATE: SELECTIVE SEPARATION OF Cd⁺⁺, Hg⁺⁺ and Pb⁺⁺ FROM SOME TRANSITION METAL IONS

S. Muzaffar Ali Andrabi

University Science Instrumentation Centre

University of Kashmir, Srinagar-190 006, J&K

(email: muzaffar2000@gmail.com, Mobile No. 09796716262)

Abstract

Titanium Phosphate, a cation exchanger, has been modified by adsorption of 1-(2-Pyridylazo)-2-Naphthol (PAN). Adsorption of several metal ions like Cr⁺⁺⁺, Mn⁺⁺, Fe⁺⁺⁺, Co⁺⁺, Ni⁺⁺, Cu⁺⁺, Zn⁺⁺, Cd⁺⁺, Hg⁺⁺ and Pb⁺⁺ on the modified ion exchanger from aqueous solutions at different pH (from 1-6) were studied to calculate their distribution coefficients. On the basis of distribution coefficients several binary separations of metal ions has been achieved on a chromatographic column packed with modified PAN-Titanium Phosphate. In addition to some binary separations selective separation of Cd⁺⁺, Hg⁺⁺ and Pb⁺⁺ from a mixture of several cations have been achieved.

ICP-89

**SYNTHESIS, SPECTROSCOPIC AND ANTIMICROBIAL ACTIVITY STUDIES ON
CHROMIUM (III) COMPLEX OF THE
BENZYLOXYBENZALDEHYDETHIOSEMICARBAZONE**

Y. Subba Rao^a, G. N. Ramesh^a, N. Nagabhusan Reddy^a, A. Varada Reddy^{a*}

^a Dept. of Chemistry, S. V. University, Tirupathi – 517502, Andhra Pradesh, India.

E-mail address: ammireddyv@yahoo.co.in

ABSTRACT

The synthesis of Cr(III) complex with benzyloxybenzaldehyde thiosemicarbazone(L) is reported in the present work. The structure of the ligand(L) is proposed based on the elemental analysis, mass, IR and ¹H - NMR spectra. The bonding and structure of the Cr(III) complex is characterized using physico-chemical and spectroscopic methods. From optical absorption spectrum of Cr(III) complex the crystal field parameters such as ligand field splitting energy(Dq) and Racah interelectroonic-repulsion parameters(B and C) are found to be 1576, 706 and 2926 cm⁻¹ indicate that Cr(III) is present in octahedral geometry. The results of the EPR studies also support octahedral geometry for Cr(III) complex as suggested by absorption studies. In order to evaluate the biological activity of ligand and its metal complex they have been screened for their antibacterial and antifungal activity against pathogenic bacteria and fungi *in vitro*.

ICP-90

**SYNTHESIS, SPECTRAL CHARACTERIZATION AND BIOLOGICAL ACTIVITIES OF
Mn(II) AND Co(II) COMPLEXES WITH BENZYLOXYBENZALDEHYDE-4-PHENYL-3-
THIOSEMICARBAZONE**

B. Prathima^a, M. Jagadeesh^a, Y. P. Reddy^b, A. Varada Reddy^{a*}

Dept. of Chemistry, S.V. University, Tirupati- 517502, INDIA

^bDept. of Physics, SPMVV Tirupati - 517502, INDIA

E-mail address: ammireddyv@yahoo.co.in

ABSTRACT

Mn(II) and Co(II) complexes of benzyloxybenzaldehyde-4-phenyl-3-thiosemicarbazone have been synthesized and characterized by the investigations of electronic and EPR spectra, X-ray diffraction and SEM. Based on the spectral studies, an octahedral geometry is assigned for the Co(II) and Mn(II) complexes. X-ray powder diffraction studies reveal that Co(II) and Mn(II) complexes have triclinic crystal lattices. When the free ligand and its metal complexes are subjected to antimicrobial activity, the metal complexes are proved to be more active than the ligand. However, with regard to *in vitro* antioxidant activity, the ligand exhibits greater antioxidant activity than its metal(II) complexes.

ICP-91

PHARMACOGNOSTIC EVALUATION OF *SYZYGium CUMINI* LINN. SEEDS USING CHROMATOGRAPHIC AND SPECTROPHOTOMETRIC TECHNIQUES

Dr. Kanchan Chitnis[#], Sachin Palekar^{*}, Dhanashri Mestry^{*}, Dhanashree Koppar^{*},

^{*}Dept. of Bioanalytical Sciences (ruiabioanal@gmail.com), [#] Dept. of Life Science, Ramnarain Ruia College, Mumbai

ABSTRACT

Introduction: India has a very rich scientific resource of traditional knowledge of herbal medicines in the Ayurveda, Unani and Siddha systems [4]. Recently, there is a shift in universal trend from synthetic to herbal medicine [1]. Plants/ Phytochemicals have been used for medicinal purposes for centuries. Dried whole plant or a specific plant part (root, leaves, fruit, flowers, seeds) is formulated into suitable monoherbal/ polyherbal preparations. Most of the plant parts of *Syzygium cumini* used in traditional system of medicine in India have promising therapeutic value due to presence of various phytoconstituents such as glycosides (jamboline), ellagic acid, gallic acid, tannins, fatty oil, steroids, flavonoids, triterpenes, phenolics, monoterpenoids, minerals, proteins, calcium and vitamins. Its pharmacological actions like hypoglycaemic, anti-diarrhoeal, antiinflammatory, antibacterial, radioprotective, antiallergic and antioxidant are proven on animal models [2, 4]. Recently, the nutritive value of jamun seeds and fruit products has been determined [3]. HPTLC method for quantification of 3-hydroxy androstane 4,5,6 H pyran, one of the marker compounds in jamun seeds has been developed and validated [4]. *In vitro* studies on the radical scavenging and anti lipid peroxidative effects of aqueous extracts of jamun seeds has also been performed [2].

Every Herbal Formulation must be standardized as per WHO guidelines, the objective of which is to define basic criteria for the evaluation of quality, safety and efficacy of drugs and herbal medicines [1].

Aims and Objectives: The primary objective of this study is to evaluate pharmacognostic parameters of jamun seeds, in which proximate analysis, total protein and tannin content are determined. The other objective is to develop an HPTLC fingerprint of different varieties of jamun seeds and possibly find a marker compound that will aid in authentication of formulations containing these.

Methods and Materials: Total proteins and tannins are estimated by spectrophotometric method (UV Vis 1700, Shimadzu). Fingerprint is obtained by HPTLC (Aetron).

Samples: Samples studied are (A) local make powder of jamun seeds, (B) formulation containing jamun seeds powder, (C) and (D) are 2 seed powders from 2 different manufacturers.

Results: Preliminary authentication of samples was done by proximate analysis as per Pharmacopoeia standards [7]. The total protein content was found to be 0.037 mg%, 0.112 mg% , 0.125 mg% and 0.045 mg% and total tannins were found to be 2.54%w/w, 4%w/w, 2.72%w/w and 3.16%w/w in samples A, B, C, and D respectively.

HPTLC fingerprint showed 3 bands with R_f values 0.15, 0.3 and 0.85 using Vanillin sulphuric acid as derivatizing reagent in all the samples, indicative of the presence of terpenoids and phenylpropanoids in the samples. HPTLC fingerprint showed 1 band common to all the samples at R_f 0.8 using Iodine vapors as derivatizing agent. HPTLC for tannins showed 4 bands in all samples at R_f 0.025, 0.225, 0.5 and 0.875 indicative of the presence of ellagic and gallic acids along with other tannins.

Future prospects: Further studies aim at isolation and characterization of the major phytoconstituents separated by HPTLC fingerprint. Therapeutic activity of these isolated phytoconstituents can also be studied using suitable animal models.

Key words: Pharmacognosy, HPTLC fingerprint, *Syzygium cumini*, tannins.

References:

- 1) A Sharma, C. Shanker, Lalit Kumar Tyagi, Mahendra Singh and Ch.V.Rao. Academic Journal of Plant Sciences 1 (2): 26-36, 2008.
- 2) F Ahmed, S Huded and F. A. Malik. Journal of Pharmacy Research, 3(1), 198-200, 2010.
- 3) M Shahnawaz, S. A. Sheikh and S.M. Nizamani. Pakistan Journal of Nutrition 8 (8): 1275-1280, 2009.
- 4) Sapana S. K., V. M. Jadhav, V.J. Kadam. International Journal of PharmTech Research, Vol.1, No.4, pp 1129-1135, 2009.
- 5) H Wagner, S Bladt. Plant Drug Analysis. CBS Publishers & Distributors, New Delhi, 2004, Appendix A.

- 6) P. Mukerjee. Quality Control of Herbal Drugs. Business Horizons, New Delhi, 2002, 325-333.
- 7) The Ayurvedic Pharmacopoeia Of India, Part I, Volume II, 87-90

ICP-92

TRACE METAL LEVELS IN THE GROWTH BANDS OF CORALS COLLECTED FROM KAVARATTI AND KILAN ISLANDS OF LAKSHADWEEP ARCHIPELAGO.

Anu Gopinath, Anuradha ,V¹ and Nair, S.M¹.

Chemistry Dept, St Teresa's College, Ernakulam

¹ Dept of Chemical Oceanography, School of Marine Sciences, Cochin

University of Science and Technology, Cochin, India

Abstract

Corals have been long recognized as marine bio-monitors, such as rainfall, runoff and upwelling events through the use of ^{18}O , Ba /Ca, Cd/Ca and Mn /Ca. In the meantime, corals have been used to monitor past sea surface temperature (SST) through chemical, Sr /Ca, U/Ca, Mg/Ca, B/Ca and isotopic ^{18}O in the aragonite skeletal lattice .Trace elements in the skeleton of tropical corals are now widely used as proxies for physical and chemical processes in the world oceans. The present work focuses on the distributional characteristics of trace metals and C-13 in the growth bands of selected coral species from two islands namely, Kavaratti and Kiltan from Lakshadweep Archipelago. The growth bands were recorded using X Radiography and from each band samples were collected by drilling. They are analysed for metals like Ca, Sr, Cd, Mn, Ni, Mg and Zn and so also for C-13.

ICP-93

EDXRF DETERMINATION OF ZIRCONIUM IN (Zr-U) MIXED OXIDES

P. J. Purohit, M.J.Kulkarni, V.Natarajan and S.V. Godbole

Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai-400085

Zirconium is an important nuclear material, in view of its low neutron absorption cross section. U-Zr alloys are being developed for reactor applications due to their excellent corrosion resistance and dimensional stability during thermal cycling. Further hydrogenated alloy phases of U-Th-Zr alloy are currently explored for use in research reactors. Generally for the determination of Zr in microgram quantities in minerals or sediments, pre-concentration by dissolution followed by solvent extraction or

precipitation using carrier like La is required. Normally zirconium content in U-Zr alloy samples is determined after dissolution of the alloy Zr followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) or spectrophotometry. EDXRF spectrometry is known to be a fast, non-destructive and versatile technique for characterisation of alloys. Earlier we had demonstrated the feasibility of EDXRF determination of Zr in aqueous solution samples, wherein the effect of the presence of uranium and/or thorium on its determination were also investigated. In the present work, the feasibility of direct determination of Zr in (Zr-U) mixed oxide powder was examined.

A series of synthetic standards containing Zr in the range 20 $\mu\text{g/g}$ to 1000 $\mu\text{g/g}$ were prepared by mixing and grinding appropriate amounts of high purity ZrO_2 and U_3O_8 powder. A Jordon Valley Ex-3600 M EDXRF spectrometer with a Rh source and liquid nitrogen cooled Si(Li) detector was used for the measurements. The measurements were done in air. In the sample chamber, the powder sample was placed in teflon cup assemblies, whose bases were fitted with thin mylar film (6.3 μm) for supporting purpose. The optimum parameters for the determination of Zr was obtained by varying X-ray tube current, voltage and counting time, using the highest standard (Rh filter, 35kV, 50 μA , 180sec.). 200 mg of each standard was used during analysis.

The plot of Zr $K\alpha$ X-ray intensity as a function of its concentration is shown in Figure 1. It may be noted that the intensity increases rapidly between 20-100 $\mu\text{g/g}$, while between 100 -1000 $\mu\text{g/g}$, the increase is less pronounced. Limited linearity was observed in the regions 20-100 $\mu\text{g/g}$ $\mu\text{g/g}$ and 100-500 $\mu\text{g/g}$, though with different slopes. This may be attributed to matrix effects. In general, the combination of matrix absorption and enhancement effects causes the calibration curves in XRF to be non-linear. In the present case, matrix absorption effect is significant, when the concentrations of the analytes exceed 100 $\mu\text{g/g}$. This may be due to the fact that when the concentration of Zr is low, the mass absorption coefficient of the analyte is essentially that of uranium and a linear relation between concentration and intensity is expected in such case. When Zr concentration increases further, the mass absorption co-efficient of the standard decreases steadily, resulting in a negative deviation from linearity due to combined effects of matrix absorption, enhancement and change in scattering of primary x-rays. The change in background near Zr $K\alpha$ rays at 15.7 keV due to strong U $L\beta$ rays at 16.4 keV is another contributing factor. By analysis of two synthetic samples, the precision of the determinations in the range 20-500 $\mu\text{g/g}$ was determined to be within 2-10%.

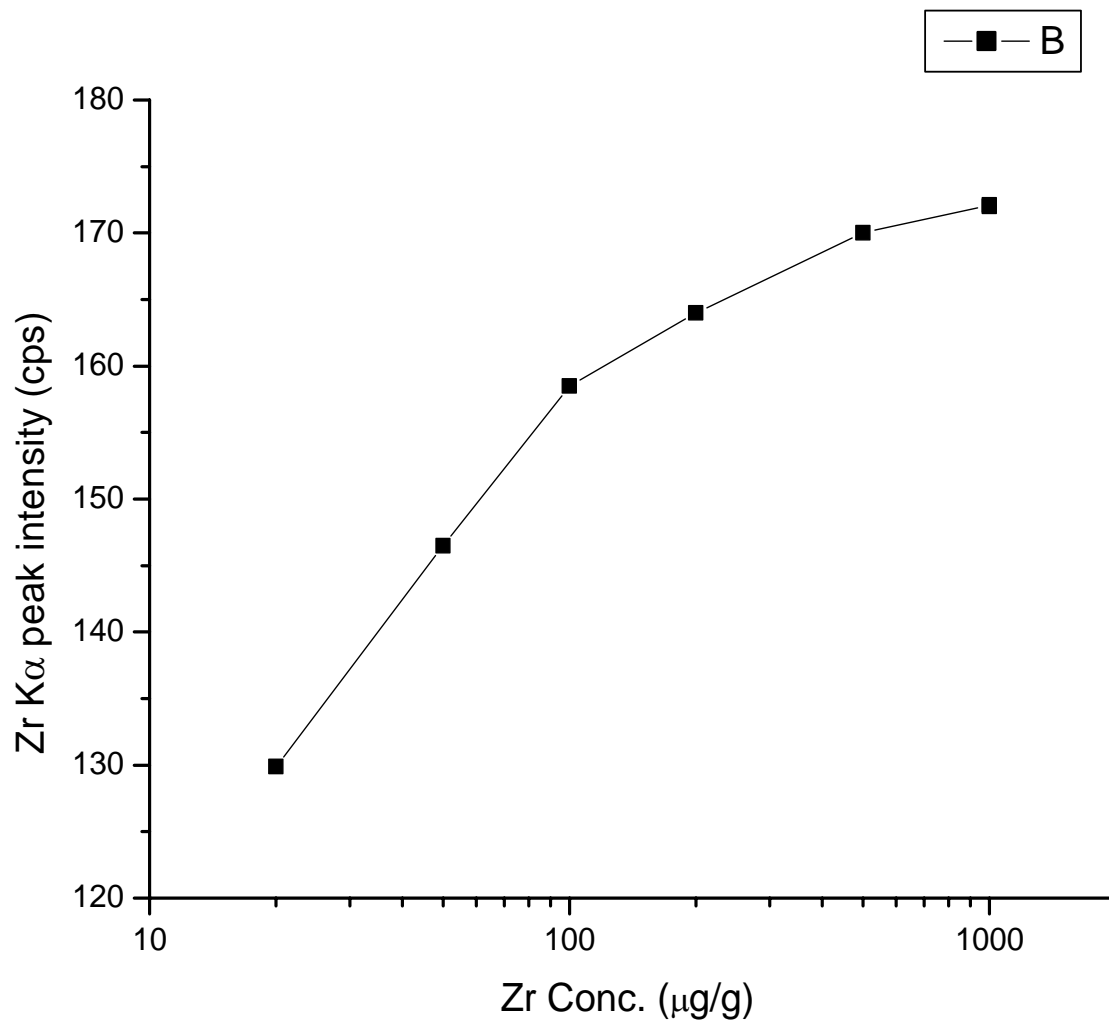


Fig.1.Variation of Zr Kα intensity (cps) with its concentration (20-1000 μg/g)

ICP-94

ANALYSIS OF SIMULATED AND HIGH LEVEL WASTE SAMPLES BY ICP-AES

S.K.Thulasidas, V.C.Adya, Mithlesh Kumar, T.K.Seshagiri* and S.V.Godbole

Radiochemistry Division, Bhabha Atomic Research centre, Mumbai – 400 085

* giritks@gmail.com

In a reprocessing plant for spent nuclear fuel, the spent fuel is dissolved in concentrated nitric acid to facilitate removal of plutonium and un-burnt uranium by suitable chemical separation process. The raffinate solution contains more than 99 % of the non-volatile fission product elements, impurities from the cladding materials, corrosion products, traces of un-separated plutonium and most of the trans-uranic elements. This reprocessing waste is called high-level radioactive liquid waste (HLLW). Such solutions are known to contain high concentration of certain elements viz: Fe (0.72 – 1) g/L, Na (3-5) g/L, Cr (0.12- 0.2) g/l, K (0.2-0.4) g/L, Mn (0.4-0.5) g/L, Sr (0.03-0.1) g/L, Ba (0.06-0.1) g/L, U (3-5) g/L, Ni (0.1- 0.2) g/L, Zr (0.004-0.02) g/L and lanthanides (present as rare earth mixture viz: Ce, La, Nd, Pr, Sm, Y etc.- (0.1-0.3) g/L. In addition few elements such as Pd, Mo, In, Sb, Se and Te have also been included as specification elements of interest in other waste solutions generated from DAE units such as IGCAR, PREFRE and BARC (WMD) etc. As a part of the work of the task force for characterization of SHLW/HLLW, methods were required to be developed by ICP-AES for determining about 25 elements such as Ag, Al, Ba, Ca, Cd, Ce, Cr, Dy, Eu, Fe, Gd, Hf, In, La, Mn, Mg, Mo, Na, Nd, Ni, Pd, Sb, Se, Sr, Sm, Y and Zr etc in such waste solutions. As these waste solutions contain appreciable amounts of Cr, Fe, Mn and Na (few % levels) contribution on the various analytical channels were monitored by aspirating 50- 500 µg/mL of these interfering elements in to ICP. It was observed that up to 200 µg/mL concentration level of the interferent, there is no significant contribution to the analytical channels of elements of interest. Few synthetic samples containing these elements were prepared and analyzed by ICP-AES after the removal of uranium by 30 % TBP in CCl₄ in 4M HNO₃ medium. For all the elements, parameters were suitably optimised to select a suitable analytical line taking in to account the relative sensitivity and interference factors. Based on the method developed samples from PREFRE, CIRUS, and FBR were analyzed. The results of two synthetic samples analyzed by the method developed for 14 typical elements are given in Table 1.

Table 1 : ICP-AES results of Synthetic SHLW samples

Elem.	Sample S-1		Sample S-2		Elem	Sample S-1		Sample S-2	
	(µg/mL)		(µg/mL)			(µg/mL)		(µg/mL)	
	Add	Estim.	Add	Estim.		Add	Estim	Add	Estim
Ba	10	10.3	20	20.2	La	5	5.2	10	5.1
Cr	8	8.6	16	15.6	Nd	5.0	4.8	10.	9.2
Cd	8	8.6	16	15.3	Ni	8	8.5	16	5.1
Cu	4.0	4.2	8.0	7.5	Pd	2.5	2.4	5.0	5.1

Dy	4	3.8	8.0	7.9	Se	10	10.4	20	19.4
Fe	50	45	100	107	Sr	4.0	3.7	8.0	6.9
In	4.0	3.8	8	8.3	Ti	2.5	2.9	5.0	4.9

ICP-95

DETERMINATION OF NOBLE METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

V.C.Adya, T.K.Seshagiri^{*}, M.K.Bhide, V.Natarajan and S.V.Godbole

Radiochemistry Division, Bhabha Atomic Research centre, Mumbai – 400 085

* giritks@gmail.com

It is well known that significant quantities of soluble fission products such as La, Ce, Pr, Eu, Gd, Sm and noble metals such as Ag, Pt, Au, Ru, Rh, Pd are produced in the spent fuel dissolver solutions, in nuclear reactors [1]. The recovery of noble metals from generated high level waste assumes importance in view of their usage in chemical and electronic industries [2]. In the present work, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) technique has been explored to determine six noble metals in aqueous solutions. Synthetic solution standards containing individually Ag, Au, Pt, Pd, Rh and Ru in the range of 1 – 500 µg/mL were prepared. Individual elemental solutions at 100µg/mL were fed in to the plasma. The instrumental parameters were obtained for positioning of the analytical line with appropriate sensitivity on the photomultiplier tube. The prominent ICP lines reported in literature in decreasing order of sensitivities for Au are 242.745, **267.895**, 197.819, **208.219** nm; Ru are 240.272, 245.657, **267.876** nm; for Rh are 233.477, **249.077**, 343.419, 252.053 nm and for Pt are **214.423**, 203.646, 214.937 nm respectively. Of these the lines shown in bold are only accessible with the axial ICP unit. used in these studies. In addition less sensitive lines in the polyscan mode were chosen, where one can access an elemental line 2.2 nm on either side of the analytical channel provided in polychromator of the instrument. The lines chosen in the polyscan are: Pt 306.471, Ru 249. 877 and Rh at 343.489 nm. For Ag and Pd the lines at 328.068 nm and 340.458 nm available with the polychromator of the ICP unit were used. A three point standardization containing the analytes in the concentration range of 0.1 to 200 µg/mL was used. The detection limits determined as per the IUPAC convention for these elements are given in Table 1 The analytical range for Ag and Pd were 0.05 – 200 µg/mL while for other elements viz: Au, Pt, Rh and Ru it was 0.5 – 500 µg/mL .

Synthetic samples containing these elements were prepared and analyzed by ICP-AES. The results of the six synthetic samples studies are included in Table 1. There is a close agreement between the amount added & the estimated amount. Energy Dispersive X-ray Fluorescence (EDXRF)

measurements were also carried out on samples S-5 and S-6 for few elements and the values obtained are reasonably in good agreement. The overall precision obtained by ICP-AES technique is within 5 % R.S.D at concentration range of < 10 µg/mL while at higher concentrations it is 1-2 % .

References

1. Chang Heon Lee, Moo Yul Suh, Kwang Sioon Choi, Jung Suk Kim, Yeong Jae Park, Won Ho Kim
Analytica Chimica Acta **475**, 171 (2001).
2. P.Petrova, S.Velichkov, N.Velitchkova, I.Havezov, N.Daskalova
Spectrochimica Acta Part **B 65**, 130 (2010).

Table 1 : ICP-AES results of the aqueous synthetic samples

Sample	Amount estimated						
	Amt.added (µg/mL)	Ag (µg/mL)	Au (µg/mL)	Pd (µg/mL)	Pt (µg/mL)	Rh (µg/mL)	Ru (µg/mL)
S-1	2.50	----	2.6	2.5	2.7	2.8	2.8
S-2	10.0	10.8	10.5	10.6	11.7	11.1	11.1
S-3	25	27.1	25.3	24.8	27.2	26.0	26.0
S-4	50	54.0	48.4	47.0	51.0	50.0	48.5
S-5	90	97.0	86.0	83.1	97.5	87.9	89.1
S-6	200	-----	185	-----	192	186	195
D.L.*		0.09	0.23	0.02	0.25	0.40	0.26

D.L = $X_{bl} + 3S_{bl}$, where X_{bl} is the mean & S_{bl} is the standard deviation of the blank measure.

ICP-96

ICP-AES DETERMINATION OF TRACE ELEMENTS IN CARBON STEEL

Arijit Sengupta, Rajeswari B., R. M. Kadam, Y. Babu and S. V. Godbole

Radiochemistry Division, Bhabha Atomic Research Centre,
Trombay, Mumbai – 400 085.

A BSTRACT

Carbon steel, a combination of the elements iron and carbon, can be classified into four types as mild, medium, high and very high depending on the carbon content which varies from 0.05% to 2.1%. Carbon steel of different types finds application in medical devices, razor blades, cutlery and spring. In the nuclear industry, it is used in feeder pipes in the reactor. A strict quality control measure is required to monitor the trace elements, which have deleterious effects on the mechanical properties of the carbon steel. Thus, it becomes imperative to check the purity of carbon steel as a quality control measure before it is used in feeder pipes in the reactor. Several methods have been reported in literature for trace elemental determination in high purity iron. Some of these include neutron activation analysis [1], atomic absorption spectrometry [2] and atomic emission spectrometry [2, 3]. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is widely recognized as a sensitive technique for the determination of trace elements in various matrices, its major advantages being good accuracy and precision, high sensitivity, multi-element capability, large linear dynamic range and relative freedom from matrix effects. The present study mainly deals with the direct determination of trace elements in carbon steel using ICP-AES. An axially viewing ICP spectrometer having a polychromator with 35 fixed analytical channels and limited sequential facility to select any analytical line within 2.2 nm of a polychromator line was used in these studies. Iron, which forms one of the main constituents of carbon steel, has a multi electronic configuration with line rich emission spectrum and, therefore, tends to interfere in the determination of trace impurities in carbon steel matrix. Spectral interference in ICP-AES can be seriously detrimental to the accuracy and reliability of trace element determinations, particularly when they are performed in the presence of high concentrations of matrix constituents. In the direct analysis of carbon steel by ICP-AES, where no prior separation of matrix is involved, spectral interference of iron on the analytes under study needs to be investigated. Therefore, a systematic study was carried out to monitor the interference effect of iron on the analytical lines of 18 elements, viz., Pb, Cd, Mn, Mo, Mg, Si, V, Cu, Ag, Ca, Na, Li, Cr, Zn, Ni, Co, B and Al. For some of the elements interference free analytical lines were identified while for the other elements, appropriate correction factors were calculated and applied to obtain final the concentration values. The method developed was used for the analysis of two carbon steel samples.

References

- [1] J. H. Zaidi, S. Waheed and S. Ahmead, *Radiochim. Acta*, **88**, 233 (2000).
- [2] J. Chen, H. Berndt, G. Tolg and J. Fresenius, *J. Anal. Chem.*, **344**, 526 (1992).
- [3] A. G. Coedo, T. D. Lopez and F. Alguacil, *Anal. Chim. Acta*, **315**, 331 (1995).

ICP-98

AMPEROMETRIC DETERMINATION OF DOPAMINE BY USING GNP-RuHCF PARAFFIN WAX COMPOSITE MODIFIED ELECTRODE

S. Anuja and S. Sriman Narayana Department of Analytical Chemistry, School of Chemical Sciences.

University of Madras, Guindy Campus, Chennai 600 025

*E-mail: sriman55@yahoo.com

Abstract

Gold nanoparticles (GNP) show easily tunable physical properties, including unique electronic properties, optical properties, robustness, and high surface areas, making them ideal candidates for developing chemical sensors and biosensors. There is an increasing demand for simple, inexpensive and rapid analytical methods to determine the concentrations of biological and environmental compounds. One such field that offers great scope is Chemically Modified Electrodes (CMEs) [1]. In recent years there has been immense interest for the fabrication, characterization and applications of modified electrodes with redox mediators such as RuHCF, NiHCF, CuHCF, CoHCF, MnHCF and Hybrid Cu-CoHCF linked with nanoparticles such as gold nanoparticles to enhance the sensitivity as well as selectivity of the modified electrodes.

As dopamine is one of the most important catecholamine neurotransmitters in mammalian central nervous system [2], it has attracted to neuroscientists and chemists. The decreased level of dopamine has been associated with painful symptoms that frequently occur in Parkinson's disease [3]. Its detection with high selectivity and sensitivity is of great significance in investigating its physiological functions.

In the present work, fabrication of paraffin wax composite electrode with GNPs and ruthenium hexacyanoferrates (RuHCF) with the help of cysteamine as cross-linker was done. The voltammetric characteristics of the RuHCF modified electrode in the presence of different alkali metal cations were investigated by cyclic voltammetry (CV). The electrode surface was characterized by scanning electron microscopy (SEM) which indicated that the RuHCF particles sized at 400-500 nm were dispersed uniformly on electrode surface. The modified electrode presents a good electrocatalytic activity toward the oxidation of dopamine. The RuHCF modified electrode is simple to prepare and this electrode shows rapid response, good stability and reproducible results.

References:

- 1) N.Oyama, F.C.Anson, J. Electrochem. Soc., 127 (1980) 249
- 2) P. Damier, E.C. Hirsch, Y. Agid, A.M. Graybiel, Brain 122 (1999) 1437.
- 3) E. Herlinger, R. F. Jameson, W. Linert, J Chem Soc Perkin Trans 2 (1995) 259

ICP-99

ESTIMATION OF ADDITIVES IN TITANIUM ALLOYS FOR SPACE APPLICATIONS BY ATOMIC ABSORPTION AND EMISSION TECHNIQUES

Jayalatha L, Deepthi L. Sivadas, , Salu Jacob, Aswathy, Rajeev R. and V.L. Rao

Analytical and Spectroscopy Division

Propellants, Polymers, Chemicals and Materials Entity

Vikram sarabhai Space Centre

Trivandrum – 695 022

arerajeev@gmail.com , r_rajeev@vssc.gov.in

ABSTRACT

The combination of high strength to weight ratio, excellent mechanical properties, resistance to high temperature and corrosion resistance make titanium and its alloys best material choice for many critical applications. Today titanium alloys are used in demanding applications like static and rotating gas turbines, space craft parts, propellant tanks, etc. The major alloying elements and minor / trace constituents in these alloys plays a major role in controlling the final properties of the material. For the development and qualification for various titanium alloys thus requires precise and accurate determination of these additives. Nowadays instrumental analytical methods like inductively coupled plasma atomic emission spectroscopy (ICP-AES), x-ray fluorescence spectroscopy (XRF), atomic absorption spectroscopy (AAS) are widely used for the fast and accurate determination of various additives, Even though XRF is a fast, and non-destructive analytical technique it is less sensitive and matrix effect is very high compared to emission and absorption techniques. Atomic emission technique using ICP-AES is having good sensitivity, high dynamic range and low matrix effect. Flame absorption technique specific, but sensitive only to limited number elements where as atomic absorption using graphite tube atomiser is highly sensitive, applicable to most of the elements , but precision is poor.

In this paper, we report the studies carried out for the quantitative estimation of aluminum, vanadium, iron, chromium, nickel and copper, some of the alloying elements / additives present in titanium alloys. Both atomic emission and atomic absorption techniques were used for the analysis. Studies were also conducted to evaluate the effect of various acids on the estimation of different additives in titanium alloy. Varying concentrations of hydrochloric acid, nitric acid, perchloric acid, sulphuric acid and nitric acid were used to prepare titanium alloy sample solutions and the additives were determined by emission and absorption techniques.

A Perkin Elmer model ICP-AES Optima 4300V was employed for the measurement of emission intensities of analyte elements. Varian model AA 280 Atomic absorption spectrometer was used for flame atomic absorption studies while Varian GTA 120 Graphite tube atomizer was employed for the atomization of analyte elements and AA 280 was employed for the absorption

measurements. Sample and standard solutions were prepared in deionised water with a conductivity of less than 0.01 μS .

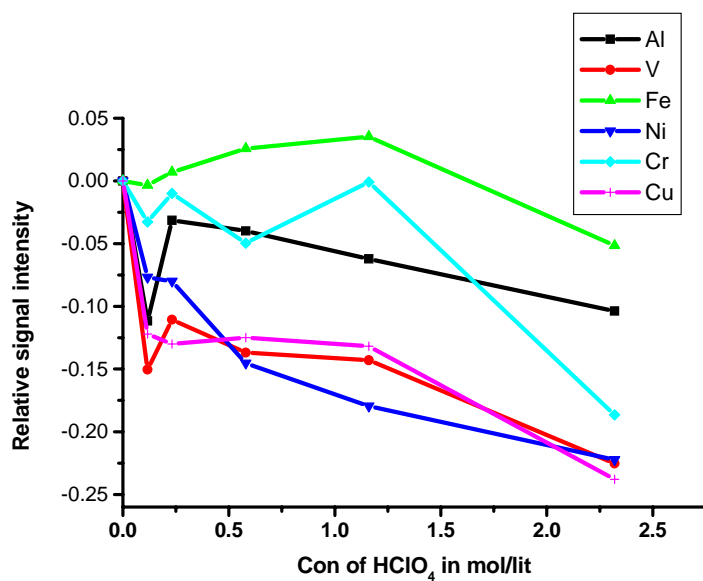


Fig. 1: Effect of perchloric acid in emission intensity of Al, V, Fe, Ni, Cr and Cu

ICP-100

CHARACTERIZATION STUDIES OF GEL GROWN CRYSTALS OF CALCIUM COMPLEX OF FOLIC ACID

Prasanna S*, Bijini BR, Deepa M¹, Rajendra Babu K, and CMK Nair

Department of Physics, M.G. College, Thiruvananthapuram-695004

¹Department of Physics, All Saints College, Thiruvananthapuram-695037

*E-mail: prasannathekkekkara@gmail.com

Folic acid or Pteroyl glutamic acid belongs to the family of Vitamin B group. It consists of a pteridine ring, p-amino benzoic acid and glutamate moiety. It is essential in the body for the formation of new cells. Both adults and children need folate to make normal blood cells. It is used in the treatment of megaloblastic anaemia [1]. It shows different ionic states with variation in pH of the aqueous solutions

[2]. Folic acid crystals precipitates in renal tubules in acidic pH. This causes intratubular obstruction which results in acute renal failure [3]. Calcium is an essential constituent of bones and plays an important role in body homeostasis. Gel is an ideal medium to grow biological crystals since its structure is similar to the mucus in the living organisms [4]. An attempt has been made to grow crystals of calcium complex of folic acid in sodium metasilicate gel medium.

Good quality crystals were formed in the gel medium of density 1.05g/cc and at a pH of 7. The grown crystals are light orange in colour. The crystals were characterized by FT-IR, XRD and CHN analysis. FT-IR spectrum reveals the functional groups present in the compound (Fig.1). The spectrum shows that the $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ for the grown crystals are changing in the same direction, i.e., in the decreasing order from the corresponding peaks in the ligand. Hence the grown calcium complex of folic acid may be bidentate. The peak at 1507cm^{-1} in the complex is due to the bending of (C-NH) group. The crystalline nature of the complex was revealed by powder XRD. The peaks found in The XRD spectrum of the complex is different from that of folic acid. Both the 2θ and d values are different from that of the ligand specifying the complexation of the sample. The chemical composition of the grown crystals was established by CHN, TGA and DTA analysis. Elemental analysis and TGA gave the composition of the complex as $\text{C}_{19}\text{H}_{17}\text{N}_7\text{O}_6\cdot\text{Ca}\cdot 8\text{H}_2\text{O}$. In TGA during the initial stage upto 340°C , 22.5% of water molecules are liberated and thereafter there is gradual elimination of gaseous parts such as CO , NH_3 , N_2 , H_2 upto 850°C . Figure(2) gives the SEM picture which clearly indicates the growth phase of the crystal.

References

- [1]. S.K.Chaudhuri. Quintessence of medical pharmacology, New central book agency (P) Ltd., Calcutta, p. 600.
- [2]. M.G.Abd El-Wahed, M.S.Refat, S.M.El-Megharbel. Spectrochimica Acta Part A, **70**, (2008).
- [3]. M.E.Huguenin, A.Birbaumer, F.P.Brunner, J.Thorhorst, U.Schmidt, U.C.Dubach, G.Thiel. Nephron, **22**, (1978).
- [4]. C.C.Desai. Crystal research and technology, **23**, (2006).

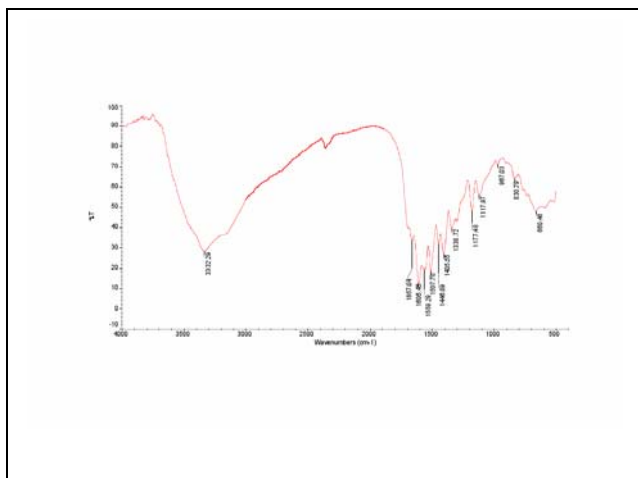


Fig.1 FT-IR spectra of Calcium complex of folic acid

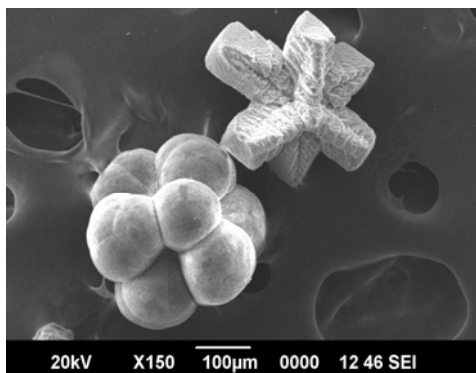


Fig.2 SEM of crystals of calcium folate complex

ICP-101

GROWTH AND CHARACTERIZATION OF STRONTIUM OXALATE CRYSTALS BY THE DECOMPOSITION OF ASCORBIC ACID IN PRESENCE OF STRONTIUM CHLORIDE

Bijini BR*, Prasanna S, Deepa M¹ and Rajendra Babu K

Department of Physics, M.G. College, Thiruvananthapuram-695004

¹Department of Physics, All Saints' College, Thiruvananthapuram-695037

Ascorbic acid (vitamin c) is an important organic compound that helps to maintain the optimal health of human body. It is essential for the development and maintenance of connective tissues. Vitamin C plays an important role in a number of metabolic functions including the activation of the B vitamin , folic acid , the conversion of cholesterol to bile acids and the conversion of the amino acid , tryptophan ,to the neurotransmitter, serotonin[1]. During the process of metabolism it decomposes into oxalic acid. This compound is photosensitive [2,3] and has least thermal stability. The decomposition of Ascorbic acid has been studied in various conditions. It is reported that decomposition of ascorbic acid in presence of Cd^{2+} ions leads to the formation of cadmium oxalate crystals [4]. In the present work, in presence of Sr^{2+} ion the ascorbic acid is decomposed to Strontium Oxalate in gel media. In this technique, silica gel is used as a medium to grow crystals. Slow diffusion of reactants in the gel medium can be considered to mimic the growth of crystals in the human body[5] . Gels were prepared by mixing appropriate quantities of sodium meta silicate and ascorbic acid, adjusting the pH in the range 5-7.5. Over the set gel, the feed solution of 1M Strontium chloride was added. Yellowish prismatic and bar shaped crystals were obtained within 24 hours. The nucleation density is maximum at a pH of 6 and minimum at 5. Good quality crystals were obtained for a pH of 5 and gel density 1.05g/cc .

SrAs(rpt)

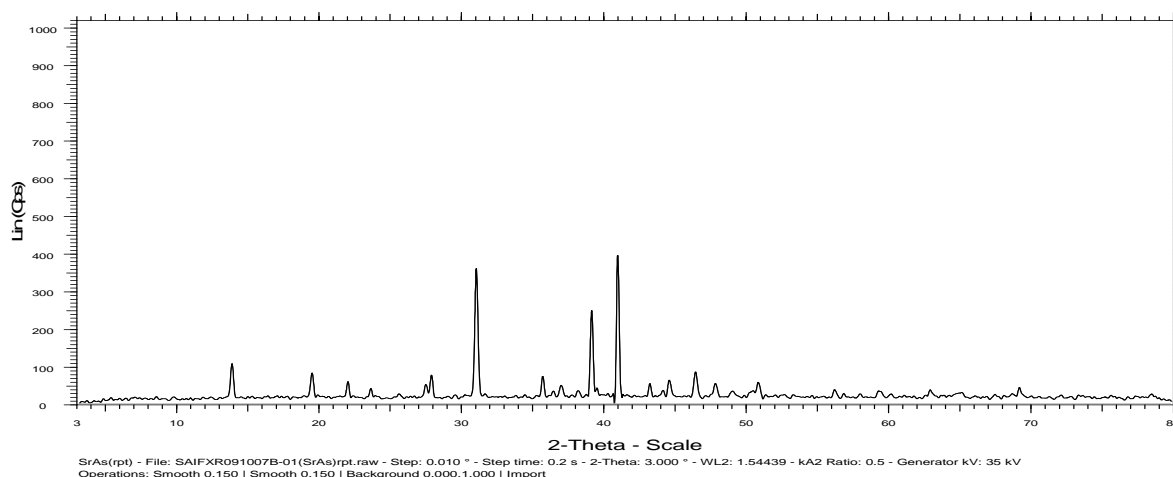


Fig 1 XRPD(powder XRD)pattern of SrC₂O₄.2.5H₂O.

Figure 1 shows the XRD pattern of the crystal grown.

The FTIR spectra of grown crystals are recorded and analyzed. The band at 3431 cm⁻¹ is assigned to OH stretching frequency of co-ordinated water molecule and the band at 1637cm⁻¹ corresponds to C= O Stretching of carbonyl group. The band at 1319cm⁻¹ is assigned to symmetric stretching of COO⁻ group. The IR band at 767cm⁻¹ corresponds to the combined effect of inplane deformation of CO₂ and the presence of metal oxygen bond .The band at 505cm⁻¹ is due to wagging mode.

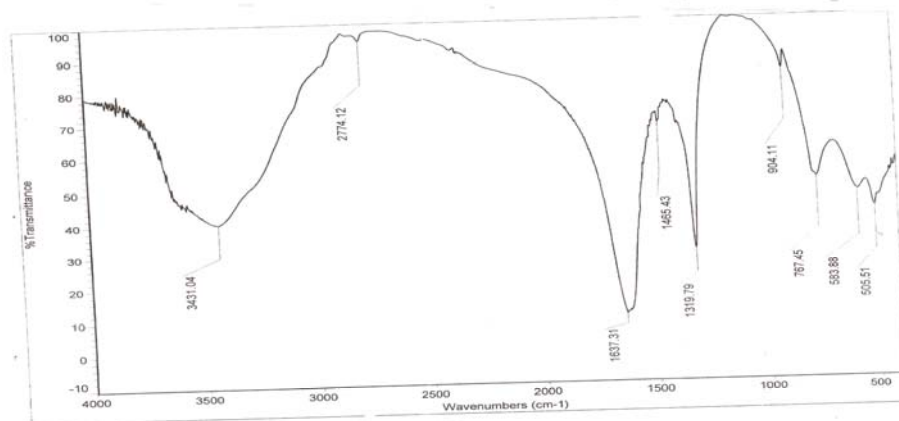


Fig.2 FT-IR Spectrum of $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$.

Thermal decomposition of the grown crystals is investigated by TGA and DTG studies. The crystals are dehydrated at around 193°C and decomposed to carbonate at 488°C .

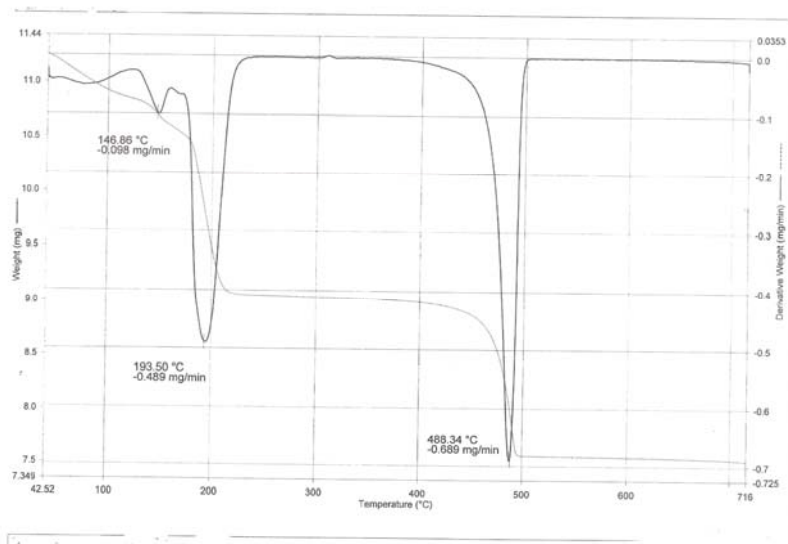


Fig.3 Thermal analysis (TGA/DTG) of $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$

The stoichiometric composition of the crystals is established by CH analysis. Results obtained from CHN analysis is compared with the theoretical value of carbon, hydrogen and nitrogen present in $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$ and given in table

Element	Composition	
	Theoretical	Measured
Carbon	10.88	10.63
Hydrogen	2.2	1.21

Calculation of the percentage weight loss from the thermo gram supplemented by CH analysis and FTIR spectroscopy suggest that the chemical formula of the grown crystal is $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$.

References

1. Khalid Iqbal , Alam Khan and M.Muzaffar Ali Khan Khattak , Pakistan Journal of Nutrition **3(1)** 5-13(2004)
2. Alexander Edwards Kellie and Sylvester Solomon Zilva ,From the Division of Nutrition , Lister Institute, London,1561-1565(1938)
3. Charles Laurence Arcus and Sylvester Solomon Zilva, From the Division of Nutrition , Lister Institute, London,61-66(1939)
4. Pierluigi Orioli, Bruno Bruni, Massimo Di Vaira, Luigi Messori and Francesca Piccioli , Inorg.Chem.**41**,4312-4314(2002)
5. K.CJoseph , B BParekh and M J Joshi 2005 Curr. Sci. **88** 1232(2005)

ICP-102

STANDARDISATION OF AYURVEDIC (OTHER TRADITIONAL/ETHNOMEDICINAL) SINGLE DRUG BOTANICALS & POLYHERBAL PREPARATIONS PART.9:ANALYTICAL QUALITY STANDARDS FOR A PROPRIETARY AYURVEDIC PAIN-RELIEVING "LEPA"(BALM/OINTMENT)

V.Vani & N.P.Damodaran*

Pain relieving balms are one of the regular OTC* pharma-products. They are claimed to relieve body pain/aches in the human system by rubbing over the local body area of pain. They contain, in general, a combination of essential oils or isolates therefrom, blended in petroleum jelly(Vaseline). A plethora of such pain balms are made by a legion of pharma companies nowadays by permutations/ combinations (& minor ingredients)in the formulae. The pain relieving machanisam in believed to be the *counter-irritant* action of the ingredients over the area of pain(sometimes described as the “rubefacient”property).

In the Ayurvedic system, selected medicated *sesame oils (Thailams)* or combinations, are in successful use from times of yore to overcome temporary pain due to sprains caused by a fall, accidental hit/blow as well as the more serious pains of the human system in diseases like arthritis & rheumatism, for which external massage (sometimes oral intake also), in conjunction with internal medicines provide relatively longer lasting healing. Standardization of any medicine modern or traditional, is a compulsory feature of GMP** ,now enforced by Drug control authorities . The Quality Standards(Q.S), enable the label claims of any medicine to be checked in an Analytical Lab and provide a “Guarantee” of Quality Assurance(Q.A) to the consuming public.

The Ayurvedic “lepa”(ointment/balm), *RHEUMAHEAL*, a proprietary medicine of the Arya Vaidya Pharmacy(Cbe)LTd, Coimbatore, offered as an OTC-product for the past 3 decades, is a blend of selected anti-rheumatic medicated oils, with counter irritant agents(mixture of essential oils/isolates) with a natural ‘lepa’ medicine, bees wax. It has enjoyed confidence and satisfaction among the users for quite some time . We report in this “poster” *Analytical Quality Standards for Rheumaheal relative to a reference sample, prepared as per label-formula*, by which, the broad composition(not of each and every individual chemical component present) can be checked . The steps are outlined below.

1. Description /organoleptic properties
2. *Routine physical parameters* - a) melting point b)moisture(as loss of wt at 110°) c)ash d) Pet.ether solubles % e) pH(10% water suspension) f)density at room temp. g)Refractive Index(molten) (h) Specific rotation $[\alpha]_D$
3. *Chemical parameters*: a) acid value b)Essential oil(E.O) content(w/w)%, as a measure of total camphor + added essential oils c) Properties of the total recovered essential oils(as a check on label contents) d) TLC profile of (total)E.O.(as a chemical fingerprint) e) GC-profile of E.O.(as Chem. Fingerprint) (f) Content(%) of non-volatiles (=medicated oils + bees-wax) g) Physico chemical properties of total non-volatiles(Acid value, Sap: Value,Iodine Value,*Unsap.matter*)(to tally with values of prepared reference sample)

The above parameters were determined under the same conditions, for a REFERENCE sample of the “lepa” from genuine ingredients prepared as per label formula and compared with those of TWO samples of “Rheumaheal” of different batches. The results will be discussed in the full POSTER.

*OTC=Over The Counter **GMP=Good Manufacturing Practices

ICP-103

**CLASSICAL INORGANIC QUALITATIVE ANALYSIS REVISITED –
SATURATED AQUEOUS POTASSIUM OXALATE AS A CONVENIENT,
INEXPENSIVE PRECIPITANT FOR SODIUM IONS.**

A.L.Satya,Priya Menon, Kaja Moideen,V.Vani, N.Natarajan and N.P.Damodaran*

International Institute of Ayurveda(Chemistry R&D), Coimbatore-641 045,

Email:avprd.ho@gmail.com

ABSTRACT

Naturally occurring Na,K(and NH₄) salts, alone, or in combination with herbal preparations find use in the Ayurvedic(& other Indian) system(s) of medicine. To cite examples only -Rock salt (NaCl),Saltpetre(KNO₃),Salammoniac (NH₄Cl). Ashes derived from medicinal plants and their aqueous leachings are also used for external and oral Ayurvedic preparations e.g. “*Apamarga Ksharam*” from *Achyranthes aspera* in “Ksharasutra” piles-therapy;*Aviltholadibhasmam* from *Holoptelia integrifolia* bark (internal).In the Quality Control of raw/”processed” Na/K/other minerals and of ash-based medicines, systematic testing for Na⁺/K⁺(& other cations), is called for

In classical schemes, groups of cations based on the insolubility of their salts, are precipitated by a *Group reagent*, the group ppt.being identified by further segregative chemistry .e.g.Gr I,Rgt;, dilute HCl, precipitates Ag⁺,Hg⁺,Pb²⁺(in part); Gr V, NH₄Cl,NH₄OH,(NH₄)₂CO₃ Rgt gives Ca²⁺,Sr²⁺,Ba²⁺. The group Na⁺,K⁺(NH₄⁺) has no *Common Group Reagent*, as all their salts are water-soluble,(a few being sparingly soluble); NH₄⁺ can be *independently* detected by release of NH₃ with caustic alkalis and in dilute aqueous solution by the brownish colour with the sensitive Nessler’s Reagent. A few reagents known to precipitate Na⁺/K⁺/(NH₄⁺) from concentrated solutions(as sparingly soluble salts) with their limitations/cross- interference are described in Standard Analysis Text Books. The more well known of these are: for Na+: 1) KH₂SbO₄ saturated 2) Magnesium uranylacetate 3) Zinc uranyl acetate 4) Dihydroxytartaric acid ; for K⁺ 1) sodium bi-tartrate(satd) 2) HClO₄ 3) H₂Pt Cl₆ 4) Na₃[Co(NO₂)₆] reagent 5) Saturated Picric acid 6) Dipicryl amine 7) Na[C₆H₅]₄ B]

The reagents for Na⁺(as may be noted) are relatively fewer. In our routine tests for K⁺, keeping in mind limitations/cross interferences, *Saturated sodium bitartrate* has been found to be satisfactory and economic . In a search for an alternative, preferably inexpensive and easily accessible precipitant for Na⁺, we have *developed a Saturated aqueous solution of potassium oxalate*, as a convenient, *hitherto unreported* (in Texts), practical reagent for Na+(comparable in efficiency to Sod. bitartrate for K⁺). This has been in successful regular use in our laboratory for several years for testing Na⁺ in Ayurvedic raw-materials, ‘processed’ minerals, med-plant –ash-medicines etc. The major limitation is that in acidic solutions , the sparingly soluble pot.hydrogen oxalate may be precipitated and mistaken for Na⁺ ions –avoidable by neutralizing with KOH..(NH₄)₂ C₂O₄ also has low solubility & may be precipitated(avoidable by pre-destroying NH₄⁺) . The test is answered by saturated solutions of most sodium salts.

With NaCl, white crystalline ppt of $\text{Na}_2\text{C}_2\text{O}_4$ is formed readily in 100%, 50%, 33% saturated solutions & on rubbing in 25% saturated solution. Details of preparation, purification, interference etc will be described in the full poster (to share our experiences with fellow-scientists)

ICP-104

ASSESSMENT OF THE AMBIENT AIR QUALITY STATUS NEAR NH-47 IN THIRUVANANTHAPURAM DISTRICT, KERALA

Jissy Jyothi S* and Jaya D. S.

Department of Environmental Sciences, University of Kerala,

Kariavattom Campus, Thiruvananthapuram, Kerala, India – 695581.

ABSTRACT

With the phenomenal growth of population, increased energy consumption, rapid urbanization and economic transformation, air pollution has reached such magnitudes that it not only threatens the health and well being of human beings and other organisms but also has potential adverse impacts at regional and global scale. Air pollution has become a growing problem in mega cities and large urban areas throughout the globe, and transportation is recognized as the major source of air pollution in many cities, especially in developing countries. Encroachment on roadsides, mixed vehicles on roads, lack of smooth traffic flow, congested and narrow roads resulting in traffic jams are some of the main causes for the vehicular air pollution. In the present study, the effect of vehicular emission on the ambient air quality has been described. A systematic ambient air quality analysis has been carried out in selected stations near National Highway-47 passing through Thiruvananthapuram district, the capital city of Kerala to evaluate the status of air pollution at traffic intersections and to find out the unique problems arising out of vehicular emissions in the study area. The ambient air samples were collected from selected stations in the study area (Kadambattukonam to Parassala) using a High Volume Air Sampler equipped with respirable dust sampler during the month of November in the year 2007, and the parameters SO_2 , NO_2 , total suspended particulate matter (TSPM), respirable and non-respirable suspended particulate matter (RSPM & NRSPM) were analyzed following the standard methods of air analysis. The traffic intensity in the study area was also monitored.

The results of the study showed that most of the air quality parameters in the study area are within the permissible limits of National Ambient Air Quality Standards during the study period except in case of TSPM and RSPM. Although the results were within the permissible limits, the concentration of particulates and gaseous pollutants in the study area increases as the vehicular intensity increases. Moreover, the concentration of NO_2 was found considerably higher than the concentration of SO_2 . Therefore from the present study it is clear that air quality in the roadside areas of Thiruvananthapuram

District is degraded due to the higher levels of pollutants especially particulates and NO₂ emitted from vehicles.

*Presenting author: jissyjyothi@gmail.com

ICP-105

ESTIMATION OF ENDOGENOUS CYANIDE IN CASSAVA USING A FLUORESCENT MOLECULAR PROBE

Kizhumuri P. Divya, Sivaramapanicker Sreejith, Palappuravan Anees and Ayyappanpillai Ajayaghosh*

Photosciences and Photonics Group, Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum, India-695019

ajayaghosh62@gmail.com

Cyanide (CN⁻) is one of the most deadly poisons, however is extensively used for gold mining, electroplating, and metallurgy to mention a few and hence is a potential threat to living systems. Moreover, cyanide tablets are widely used by fishermen for the capture of fish and hence cyanide detection in fish samples is important. Many plants are known to contain endogenous cyanides which is again a potential source of CN⁻ poisoning to living systems. For example, Cassava (*Manihot Esculenta*) which is a cheap source of food in tropical countries contains a large amount of cyanogenic glycosides, which either spontaneously or enzymatically release hydrogen cyanide. Eating of fresh cassava tuber and leaves is therefore dangerous to animals. Herein, we report the use of a fluorophore **3**, and its fluorescent zinc complex **4** for the detection of endogenous cyanide content in natural products which will help quality control in Cassava based food products.[1,2]

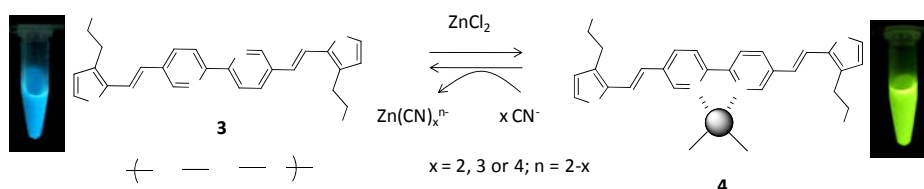


Figure 1. A cation displacement protocol for the detection of CN⁻ using the fluorescent probe **4**.

Bipyridines conjugated with heterocyclic end functional moieties selectively form fluorescent complexes with Zn²⁺ whereas other transition metal ions form nonfluorescent complexes. Replacement of zinc complex with CN⁻ regenerate the initial fluorescence of the probe, thereby allowing ratiometric detection of the latter. Practical application of the probe is demonstrated by screening the endogenous cyanide content in the latex of Cassava, Papaya and Mango in which only Cassava latex showed response.

References

1. K. P. Divya, S. Sreejith, B. Balakrishna, P. Jayamurthy, P. Anees and A. Ajayaghosh *Chem. Commun.* DOI:10.1039/C0CC01159B.,(2010).
2. A. Ajayaghosh, S. Sreejith, K. P. Divya and P. Jayamurthy, Ind. Patent Appl. 122NF/2009.

ICP-106

COMPARITIVE CATALYTIC EFFICIENCY BETWEEN ADSORBED AND COVALENTLY BOUND GLUCOAMYLASE ON MESOPOROUS SILICA

Reni George, S. Sugunan*

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-682022, Kerala, India. Tel: + 91-484-2575804. Fax: +91-484-2577595, Email: ssg@cusat.ac.in, renivgeorge@gmail.com

Abstract:-

Mesoporous silica was synthesized by hydrothermal procedure using tetraethylorthosilicate (TEOS), amphiphilic block co-polymers Pluronic P123 and n-decane as auxiliary chemical under acidic conditions [1]. The amino groups have been grafted to as-synthesized mesoporous silica by 3-aminopropyl trimethoxysilane (3-APTS) [2]. The physicochemical properties of these prepared materials were characterized by Small angle XRD, Nitrogen adsorption – desorption, FTIR, TG/DTG, and SEM experiments. Comparison between adsorbed and covalently bound glucoamylase on mesoporous silica has been studied. Covalently immobilized glucoamylase shows higher catalytic efficiency than adsorbed glucoamylase. . It is clear that surface morphology is very important on the immobilization of enzyme.

References:-

- [1] Suman.K.Jana, Reiichi Nishida, Micropor. Mesopor. Mater., **68**,133-142 (2004)
- [2] Priti H. Pandya, Raksh V. Jasra, Micropor. Mesopor. Mater., **77**, 67-77(2005)

ICP-107

STUDIES ON THE DETERMINATION OF TRACE AMOUNT OF URANIUM IN PLUTONIUM PRODUCT SOLUTION BY ICP-AES

G. Mary, K.Radhakrishnan, S.C. Tripathi, S.K. Munshi and P.K. Dey

The present paper describes an analytical method for the determination of trace amount U in the presence of large quantities of Pu employing Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). In the PUREX process, the U content in the final Pu product solution is an important parameter for ascertaining the recovery of Pu from U. Generally, U in Pu product solution is determined by spectrophotometric methods^[1]. If U is present in large quantities along with Pu, a direct estimation by ICP-AES can be adopted^[2]. In present work, studies on spectral interferences of Pu on the highly sensitive U spectral wavelength 385.958 nm showed a tolerance of up to 50 µg/ml of Pu. Hence, it was mandatory to separate Pu from the samples prior to ICP-AES analysis. Pu was separated by precipitation as oxalate using oxalic acid. Since the supernatant contains some oxalic acid, the effect of oxalic acid on the U spectral line showed an enhancement of the spectral background above a concentration of 0.01M. Therefore, the excess oxalic acid in the supernatant was kept at 0.01M.

All compounds and reagents used were of high purity. Suitable aliquots of Pu solutions containing varying amount of Pu were treated with oxalic acid to ensure near complete precipitation. The supernatant along with washing was analysed for U and Pu using wavelengths 385.958 nm and 300.060 nm respectively. The residual Pu in all the supernatants was less than 10 µg/ml. Similar experiments were carried out with simulated Pu samples containing U at varying concentration levels. The results obtained are given in Table 1. The recovery of U for the concentration levels studied varied between 94% - 104% and it could be determined with a precision of $\pm 5\%$. This method has applicability in determination of U in Pu rich Purex process streams.

Table 1. Recovery of U at varying concentrations

Pu content mg	U spiked µg	U determined µg	Recovery of U (%)
5	5	5.16 \pm 0.16	102
5	10	9.82 \pm 0.22	98
10	5	4.80 \pm 0.21	96
10	10	9.36 \pm 0.18	94
15	5	5.21 \pm 0.09	104
15	10	9.66 \pm 0.28	96

References

1.S.K.Das, S.G. Rege, A.Mukherjee, A.Ramanujam, R.K.Dhumwad,.BARC Report, 1539(1991).

2.D.K.Pant,G.A.Chaugule,B.A.Bhalearo,K.K.Gupta,P.G.Kulkarni,P.B.Gurba,P.Janardan,

R.D.Changrani, P.K.Dey. Symposium on Role of Analytical Chemistry in Nuclear

Technology, 194(2007).

IMMOBILIZATION OF DIASTASE ALPHA- AMYLASE ON CHEMICALLY PREPARED MESOPOROUS POLYPYRROLE

Navya Antony, P.V. Mohanan**

Department of Applied Chemistry, Cochin University of Science & Technology, Kochi-22,India

** Correspondence, [E-mail: mohan@cusat.ac.in](mailto:mohan@cusat.ac.in)

ABSTRACT

Enzyme engineering is a fast-growing application in the pharmaceutical market. Enzymes are key to new processes because they are environmentally friendly and reduce hazardous waste. Enzymatic reactions can occur under milder conditions, at a faster rate, while being highly specific. Therefore, enzymatic process allows to minimize process steps. Immobilized enzymes enhance process robustness, allow longer duration of activity of enzymes, and re-use of the same enzymes in multiple cycles. Further more, the use of immobilized enzyme eliminate the enzyme separation step from the main process thus simplifying and increasing the overall process yield thus lowering the total production cost of enzyme mediated reactions. Amylases are among the most important hydrolytic enzyme for all starch based industries. In this study alpha amylase was adsorbed on to mesoporous polypyrrole synthesized by chemical polymerization using commercial colloidal silica salt particles as templates [1]. Among the conducting polymers known to date, ones based upon PPy have attracted special interest because of their high conductivity, their ease and high flexibility in preparation, their good environmental stability and good mechanical properties[4].We have prepared mesoporous polypyrrole to increase the surface area of polypyrrole[2,3]. Mesoporous polypyrrole and enzyme immobilized samples were characterized by IR ,SEM, UV, XRD, TG and surface area measurements . Immobilization was performed successfully under room temperature. The immobilized alpha amylase exhibited better optimum reaction temperature and thermo stability than native enzyme. The effects of pre-incubation time, reaction pH and enzyme loading on the support were studied. The kinetic parameters V_{max} and K_m were determined for both immobilized and native enzymes. The pH profile of immobilized and free enzyme showed almost similar behaviour with optimum activity in the range of pH 5 to 6. Leaching, storage stability and reusability studies of immobilized enzyme shows that alpha amylase retains its activity for several cycles where as free enzyme lost almost complete activity within 10 days.

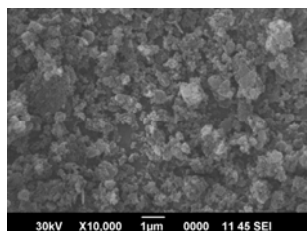


Figure: SEM Image of polypyrrole prepared in presence of colloidal silica particles

REFERENCES

1. Kim Sunghyun, Jang Jyonsik, Applied Chemistry, **Vol.9**, No.1, 269-272 (2005)
2. Youngnam Cho¹ and Richard Ben Borgens¹, NanoTechnology **Volume 21**, Number 20
21 205102 (2010)
3. Liangming Wei, Nantao Hu and Yafei Zhang Materials **Vol. 3**, 4066-4079 (2010)
4. Reza Ansari, E-Journal of Chemistry, **Vol. 3**, No.13, pp 186-201, (2006)

ICP-109

USE OF VARIOUS ANALYTICAL TECHNIQUES IN THE VALUE ADDITION OF KAOLIN – A CASE STUDY

S.Ramaswamy and P.Raghavan

National Institute for Interdisciplinary Science and Technology (NIIST),
CSIR, Govt. of India, Thiruvananthapuram-695 019, India
Phone : +91-471-2515310; Fax : +91-471-2491712, E-mail : che_swamy@niist.res.in

Abstract

Kaolin or china clay is a versatile industrial mineral. The major mineral in kaolin is kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The common impurities are quartz, titaniferous, ferruginous, micaceous, carbonaceous and sulphide minerals and these impurities are to be removed to achieve specific particle size and good brightness. Kaolin finds extensive applications in paper, paint, rubber, ceramics, plastics etc. The specifications may be different, but stringent for each application. The versatility of kaolin in its applications is due to its unique properties like layered and platy structure, whiteness, chemical inertness, typical morphology, fine particle size etc. One of the highest value addition in its application is as pigment in paper and paint industries. Characterization followed by beneficiation is essential not only to prevent its underutilization but also to give value addition to the mineral. Also, the identification and quantification of the impurities plays an important role in the selection and sequentialisation of beneficiation processes. At every stage of beneficiation, the feed, the intermediates and products are to be characterized for developing the beneficiation flow sheet. This shows that the use of various analytical tools has got an important role in the beneficiation/value addition and industrial utilization of kaolin.

One of the most deleterious impurities in kaolin is iron minerals which imparts colour to the white kaolin. Even the presence of low concentrations of iron minerals will adversely affect the

optical properties of kaolin. The optical properties are stringent for pigment applications and removal of the “Fe” impurity is very important. Iron may present as a part of the kaolinite or ancillary mineral (mica or titania) structure i.e., “structural iron” or as separate iron minerals such as oxides, hydroxides, oxy-hydroxides, sulphides and carbonates i.e., “free iron” [1]. The preliminary step of beneficiation is size classification using a set of hydrocyclones to remove the coarser impurities. The coloured ultrafine impurities can be removed by employing techniques such as Superconducting High Gradient Magnetic Separation, Ultra flotation and Oxidative/Reductive bleaching. The Citrate Dithionite Bicarbonate (DCB) treatment gives information on the quantity of “free iron” which can be removed by chemical leaching.

The physical, chemical, mineralogical, morphological and spectroscopic analysis of kaolin and ancillary minerals give basic information on the constituents and structural and other properties of the clay. Various analytical techniques are used to (i) identify and quantify the kaolinite and the associated minerals in order to select and sequentialise the beneficiation techniques for value addition and (ii) to characterize the beneficiated product for specialized applications. X-ray diffraction (XRD) and thermal analysis (DTA/TGA) give the mineralogy. The structural order/ disorder which can also be studied by FT-IR. The morphology (size and shape) of the particles is determined by electron microscopy (SEM/TEM). Chemical analysis by wet chemical methods supported by instrumental techniques [UV-Visible, Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)] gives the major and minor/trace elements in clays. Unlike in many other fields, the results here are reported as the percentage of oxides in order to give a truer picture of the material. Also, rational analysis is usually carried out by calculating the mineral content from the chemical composition.

Impurity mineral identification and their removal are the two important aspects in the value addition of kaolin. The advent of sophisticated spectroscopic analytical techniques has made it easy to understand the state of iron and its effect on the properties of kaolin [2]. The crystallo-chemical characteristics and the assembly of kaolinites with the associated iron oxyhydroxides are closely linked to the geological conditions in which the kaolins are formed. Iron minerals in kaolin are often found to be of low concentrations, having different particle sizes and sometimes they are found to be more or less amorphous in nature. The difficulties associated with the low concentration of iron in kaolin, the complexity of the natural material matrix from which kaolins are obtained and the effect of pre-concentration or extraction methods often require the use of multiple advanced analytical techniques to characterize the materials. In addition to X-ray Diffraction Analysis (XRD), the traditional tool for mineral identification, advanced analytical techniques like Electron Paramagnetic Resonance Spectroscopy (EPR), Moss Bauer spectroscopy, Infrared Spectroscopy can be used to identify the nature of iron present (free or structural), crystal defects, the oxidation state of the iron present etc. Electron Probe Micro Analysis (EPMA) of the sample gives the distribution of elements on the particles. High Resolution Transmission Electron Microscopy fitted with Energy Dispersive Spectroscopy (HR-TEM EDS) can be used to carry out the atomic level microanalysis of the samples.

The present paper deals with the various analytical techniques (chemical, physical, mineralogical, morphological and spectroscopic) used for characterizing a typical kaolin sample (and its beneficiated products) collected from Kutchh District of Gujarat State. The paper also highlights the role played by various analytical techniques in identifying and quantifying the impurity mineral species

present in the kaolin sample. The chemical and mineralogical analysis have shown that kaolinite is the major mineral present in the sample. The DCB treatment and EPR spectral studies indicates that most of the iron in the sample is in the structural form. Spectroscopic (Mossbauer) and microscopic (HRTEM-EDS) analysis of the impurity minerals separated from the kaolin sample have shown that the major impurity mineral phase present in the sample is in "titaniferous" form. Though pure TiO_2 does not absorb light in the visible region, it strongly absorbs in the UV region due to the metal oxygen charge transfer process. When iron is present in the structure of TiO_2 , a Fe(II) Ti(IV) transition is possible. When "Fe" and "Ti" are present together in a glass, a charge transfer or electron hopping process takes place between "Fe" and "Ti" ions via an intermediate oxygen ion [3]. This charge transfer process has an absorption centered at 350 nm in the near UV region tailing into the visible at the blue end of the spectrum. Intensities of charge transfer bands are reported to be 100-1000 times stronger (in terms of extinction coefficient) than other transitions like d-d type, so a small quantity of iron can make a major adverse effect on the shade of the kaolin ('Titania effect') [4]. The impact of the "titania effect" will be more pronounced, as the brightness (capacity of the material to reflect the light in the visible region) of kaolin is measured at 457 nm. In the present study, the identification and quantification of the 'structural iron" phase present in the sample has played a crucial role in selecting and sequentialising the beneficiation process. Also, evaluation of the properties (chemical assay, particle size distribution and brightness) of the product sample has shown that the kaolin sample can be value added to paper coating grade.

References

- [1] Jepson, W.B., 1988. Structural iron in kaolinites and in associated ancillary minerals, In : Iron in Soils and Clay Minerals (J.W.Stucki, B.A.Goodman and U.Schwertmann, editors).NATO Advanced Science Institutes Series, D.Riedel Publishing Company, Dordrecht, Holland, pp. 467-53.
- [2] Brindley, G.W., Kao,C.C., Harrison, J.L., Lipsicas, M., and Raythata, R.,1986. Relation between structural and other characteristics of kaolinite and dickite. Clay and Clay Minerals, 34, pp. 239-249.
- [3] Hogg C.S., Noble F.R. (1979). A Kubelka - Munk analysis of the influence of iron and titanium oxides on the optical properties of hard porcelain, Science of Ceramics, Volume 10, Berchtesgaden, Germany, 703-710.
- [4] Weaver C.E. (1976), The nature of TiO_2 in kaolinite, Clays and Clay Minerals, 24, 215-218.

ICP-110

THEMOGRAVIMETRIC ANALYSIS OF COPOLYMER RESIN

**DERIVED FROM P-NITROPHENOL, TRIETHYLENETETRAMINE
AND FORMALDEHYDE**

Pawan P. Kalbende, Anil B. Zade

Department of Chemistry, Laxminarayan Institute of Technology, Rashtrasant
Tukdoji Maharaj, Nagpur University, Nagpur-440 010, India.
E-mail: ab_zade18@yahoo.com

Abstract

Copolymer (NPTETAF-I) has been synthesized by the condensation of monomers namely, p- nitrophenol (p-NP), triethylenetetramine (TETA) and formaldehyde (F) in presence of sodium hydroxide (2M) as a catalyst by taking ratio of reactants 4:1:8. The composition has been determined on the basis of their elemental analysis and further characterized by spectral studies such as UV-Visible absorption spectra in nonaqueous medium, Infra-red (IR) spectra and nuclear magnetic resonance (NMR) spectra. Emphasis has been given on thermal studies of the resin to determine their mode of decomposition. The Freeman Carroll and Sharp Wentworth methods have been used to calculate thermal activation energy and thermal stability which were found to be in agreement with each other. The activation energy (E_a), order of reaction (n), frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy change (S^*) have been calculated.

References:

1. R. N. Singru, A. B. Zade, W. B. Gurnule Journal of Applied polymer science, Wiley Periodicals, Inc.(U.S.A.), **109(2)**, 859-868 (2008).
2. M. V. Tarase, A. B. Zade, W. B. Gurnule Journal of Applied Polymer Science, Wiley Periodicals, Inc.(U.S.A.), **116**, 619-627 (2010).
3. S. S. Butoliya, W. B. Gurnule, A. B. Zade e-Journal of chemistry, **7(3)**, 1101-1107 (2010).

ICP-111

**SYNTHESIS AND CHARACTERIZATION OF NEW COPOLYMER RESINS DERIVED
FROM P-NITROPHENOL, TRIETHYLENETETRAMINE AND FORMALDEHYDE**

Pawan P. Kalbende, Mangesh V. Tarase, Anil B. Zade

Department of Chemistry, Laxminarayan Institute of Technology, Rashtrasant Tukdoji Maharaj, Nagpur University, Nagpur-440 010, India.

E-mail: ab_zade18@yahoo.com

ABSTRACT

Copolymer resin NPTETAF-I has been synthesized by condensation polymerization reaction of monomers namely p-nitrophenol (p-NP) and triethylenetetraamine (TETA) with formaldehyde (F) using molar proportions 4:1:8 in alkaline media. Various important properties like solubility in various common organic solvents; viscosity measurements; number average molecular weights (\overline{M}_n) by using appropriate techniques have been studied. Elemental analysis studies were carried out for the determination of empirical formula. Studies were further extended to spectral analysis such as UV-visible, FT-IR and ^1H NMR to confine the most probable structure of designed copolymer.

References:

1. M. V. Tarase, A. B. Zade, W. B. Gurnule, J. App. Polym. Sci., **108(2)**:738. (2008)
2. R. H. Gupta, A. B. Zade, W. B. Gurnule Journal of Applied Polymer Science, Wiley Periodicals, Inc.(U.S.A.),**109**, 3315– 3320, (2008).
3. S. S. Rahangdale, W. B. Gurnule, A. B. Zade. Indian journal of Chemistry, **48A**, 531-535, (2009).

ICP-112

SYNTHESIS AND CHARACTERIZATION OF CO-POLYMER RESIN (ASAOF-I) DERIVED FROM P-AMINOSALICYLIC ACID, OXAMIDE AND FORMALDEHYDE

Rahul N. Shrungare, Suraj S. Butoliya, Anil B. Zade

Department of Chemistry, Laxminarayan Institute of Technology, Rashtrasant Tukdoji Maharaj, Nagpur University, Nagpur-440 010, India.

E-mail: ab_zade18@yahoo.com

ABSTRACT

Monomers namely p-Aminosalicylic-acid (p-ASA), Oxamide (O) and Formaldehyde (F) were used in molar proportion 1:1:2 by condensation polymerization at 160 °C in basic medium to synthesize copolymer resins ASAOF-I. Solubility behavior after purification of newly synthesized co-polymer was examined in protic as well as aprotic solvents. Number average molecular weights (\overline{M}_n) have been determined by conductometric titration and viscometric measurements in nonaqueous medium. Formation of copolymers has been further confirmed by using various physico-chemical methods like elemental analysis and spectral techniques like ultraviolet-visible, fourier transform-infra red, proton nuclear magnetic resonance spectra to suggest the most probable structure of these copolymers.

References:

1. R. N. Singru, W. B. Gurnule, A. B. Zade. Journal of Applied Polymer Science , Wiley Periodicals, Inc.(U.S.A.),**116(3)**,1400-1407,(2010)
2. S.S. Katkamwar, A. B. Zade, S. S. Rahangdale, W.B. Gurnule. Journal of Applied Polymer Science, Wiley Periodicals, Inc.(U.S.A.),**113**, 3330 – 3335, (2009).
3. S. S. Rahangdale, A. B. Zade, W.B. Gurnule. Journal of Applied polymer science, Wiley Periodicals, Inc.(U.S.A.),**108(2)**,747-756 (2008).

ICP-113

STUDIES OF TERNARY COMPLEX FORMING SYSTEMS OF HOLMIUM(III) AND LUTETIUM (III) WITH PYROGALLOL RED IN PRESENCE OF CETYLPYRIDINIUM BROMIDE FOR MICRODETERMINATION

A. B. Zade and A. S. Dhepe

Department of Chemistry, Laxminarayan Institute of Technology, Rashtrasant Tukdoji Maharaj, Nagpur University, Nagpur-440 010, India.

E-mail: ab_zade18@yahoo.com

Abstract

Pyrogallol red has been reported to form blue colored complexes with lanthanides and has been used for microdetermination of these metal ions. In the present investigation, it has been observed that the addition of cationic surfactant, cetylpyridinium bromide (CPB), sensitizes the color reactions of Ho (III) and Lu (III) with pyrogallol red. The formation of highly colored water soluble ternary complex of stoichiometric ratio 1:1:4 (Ln(III)-R-CPB) is responsible for the observed increase in molar absorptivity at shifted wavelength, when a surfactant is present. The ternary complexes exhibit bathochromic shift of about 35nm for both the metal ions under study. Beer's law obeyed between 0.5 to 6.30 ppm. Effective photometric range and molar absorptivity of these ternary complexes have been calculated. The optimum reaction conditions and other analytical parameters were evaluated. The effects of interfering ions on determination of both the metal ions were studied. A simple, rapid and highly sensitive method for the determination of Ho (III) and Lu (III) with pyrogallol red is proposed.

References :

- A. S. Dhepe, A. B. Zade Analytical chemistry- Indian Journal, **10(2)**, 215-221 (2010).

ICP-114

**GROWTH AND CHARACTERIZATION OF A NEW SEMIORGANIC NON LINEAR
OPTICAL CRYSTAL:LEAD SUCCINATE MONOHYDRATE**

V.S. Dhanya, M.R. Sudarsana Kumar, Sunalya M.Roy

Department of Chemistry, M.G. College, Thiruvananthapuram 695 004,

Kerala, India.

ABSTRACT

Organic and semi organic non linear optical (NLO) materials have been intensely investigated due to their potentially high non linearities and rapid response in electro-optic effect. In the last decade, organic (NLO) crystals with aromatic rings have attracted much attention because of their high non linearity, fast response and tailor made flexibility. However the shortcomings of aromatic crystals, such as poor physicochemical stability, low hardness and cleavage tendency hinder their device application. In order to keep the merits and overcome the short comings of organic materials, some classes of NLO crystals such as metal organic or semiorganic crystals have been developed [1,2]. Semi organics are formed by combining organic molecules of high polarizability with mechanically strong and thermally stable inorganic molecules. These materials combine the chemical flexibility and nonlinearity of organics and favourable physical properties of inorganics. In recent years there has been considerable interest in the study of semi organic NLO crystals with good non linear properties because of their wide applications in the area of laser technology, optical communication, optical information processing and optical data storage technology. Lead Succinate monohydrate is such a semi organic non linear optical (NLO) crystal with molecular formula $[Pb(C_4H_4O_4)]H_2O$. In the present investigation, we report the growth of Lead Succinate Monohydrate by gel diffusion technique. Sodium Meta Silicate was used for gel preparation[3]. The crystals were characterized using powder and single crystal X-ray diffraction studies, Fourier transform infrared (FT-IR) analysis, FT-Raman, UV-visible transmittance studies, Thermo Gravimetric Analysis and Differential Thermal Analysis (DTA). Dielectric constant and dielectric loss of the grown crystals were also evaluated.

Single crystals of Lead Succinate Monohydrate $[\text{PbC}_4\text{H}_4\text{O}_4] \cdot \text{H}_2\text{O}$ have been successfully grown by gel diffusion technique. The crystallinity of the grown crystals has been analysed by powder X-ray diffraction studies. Single crystal X-ray diffraction analysis shows that they belong to monoclinic system. Fourier transform infrared (FT-IR) and Fourier transform Raman (FT-Raman) spectral studies have been performed to identify the functional groups. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were used to study its thermal properties. The optical transmittance window and the lower cut off wavelength of the crystal have been identified by UV-visible transmittance studies. Dielectric constant and dielectric loss of the grown crystals were evaluated for the frequency range 300 Hz- 3 MHz. The second harmonic output intensity was tested using Kurtz and Perry powder method and was 3.5 times as large as KDP.

KANYAKUMARI, THE SOUTHERN MOST TIP OF INDIA



Vivekananda Rock Memorial ,Kanyakumai

Kanyakumari or Cape Comorin, the southern most tip of peninsular India, is the confluence point of southern most tip of peninsular India, is the confluence point of three oceans - the Bay of Bengal, the Arabian Sea and the Indian Ocean. Apart from this, it is renowned for its exotic sunrises and sunsets over the horizon. One of the unique features of Kanyakumari is the multicolored sand found on its beach. Tourist attractions: Swami Vivekananda rock; Gandhi Memorial (Mahatma's ash was kept for public viewing before submersion); Thiruvalluvar statue (133 ft) etc.



Thiruvalluvar Statue-Kanyakumari

REACH KANYAKUMARI

By Air : The nearest airport from Kanyakumari is situated at Trivandrum about 80 km away. Trivandrum is directly connected with Bangalore, Mumbai, Cochin, Delhi, Goa, and Chennai by regular flights.

By Rail : Kanyakumari is well connected by rail to major parts of the country by broad-gauge railway network. Superfast trains connect the southern most railhead of India with all major cities in India

By Road : Kanyakumari is connected by road to Trivandrum (86 km), Nagarkoil (19 km), Tirunelveli (91 km), Tiruchendur (89 km), Tuticorin (129 km), Rameshwaram (300 km), Courtallam (130 km), Madurai (242 km), Thekkady (358 km), Kodaikanal (362 km), Palani (370 km), Ootacamund (576 km), Cochin (309 km) and Coimbatore (478 km).



Mahatma Gandhi Memorial-Kanyakumari