3.3.1 Number of research papers published per teacher in the Journals notified on UGC Care list during the last five years

Sr. No	Title of paper	Name of the author/s	Department of the teacher	Name of journal	Year of publication	ISSN number	Link to the recognition in UGC enlistment of the Journal /Digital Object Identifier (doi) number		
							Link to website of the Journal	Link to article / paper / abstract of the article	Is it listed in UGC Care list
1	Ion-pair based liquid--liquid extraction of gold (III) from malonate media using 2-octylaminopyridine as an extractant: analysis of alloys, minerals, and drug samples	V Suryavanshi, A Kokare, S Zanje, A Mulik, R Pawar, M Patil, A Gaikwad, M. Anuse, G. Mulik	Chemistry	Turkish Journal of Chemistry	2018	ISSN: 1300-0527	https://journals.tubitak.gov.tr/chem/	https://journals.tubitak.gov.tr/chem/vol42/iss4/7/	Yes
2	2-Nitrobenzaldehyde Thiocarbohydrazone Assisted Precise Extraction Spectrophotometric Method for the Determination of Ruthenium (III) in Alloy and Catalysts	SB Zanje, VJ Suryavanshi, AN Kokare, AA Ghare, GS Kamble, PN Kamble, MA. Anuse	Chemistry	Journal of Analytical Chemistry	2018	Electronic ISSN 1608-3199 Print ISSN 1061-9348	https://www.springer.com/journal/10809	http://link.springer.com/article/10.1134/S1061934818050131	Yes
3	Gold ions mediated diproline peptide nanocarpets inhibits bacterial growth	Singh R.; Suryavanshi V., Vandana Vinayak, Joshi K. B.,	Chemistry	ChemistrySelect	2019	Online ISSN:2365-6549	https://chemistry-europe.onlinelibrary.wiley.com/journal/23656549	https://doi.org/10.1002/slct.201900847	Yes
4	Highly proficient extraction separation of thorium(IV) from sulfuric acid solution using N-n-decylaniline: real sample analysis	Makrand M. Patil · Vishal J. Suryavanshi, Abhijeet G. Mulik, Ganpatrao N. Mulik	Chemistry	Journal of Radioanalytical and Nuclear Chemistry	2020	Electronic ISSN 1588-2780 Print ISSN 0236-5731	https://www.springer.com/journal/10967	https://doi.org/10.1007/s10967-020-07204-7	Yes
5	Liquid–liquid extraction of uranium(VI) from weak sodium acetate medium using 2-octylaminopyridine: real sample analysis	Gurupad D. Kore, Sunil B. Zanje, Arjun N. Kokare, Vishal J. Suryavanshi, · Mansing A. Anuse, Sanjay S. Kolekar	Chemistry	Journal of Radioanalytical and Nuclear Chemistry	2021	Electronic ISSN 1588-2780 Print ISSN 0236-5731	https://www.springer.com/journal/10967	https://doi.org/10.1007/s10967-021-07828-3	Yes
6	Amorphous nickel tungstate films prepared by SILAR method for electrocatalytic oxygen evolution reaction	D.B. Malavekar a, V.C. Lokhande b, D.J. Patil c, S.B. Kale a, U.M. Patil a, T. Ji b, C.D. Lokhande a	General Engineering	Journal of Colloid and Interface Science	2022	Science Direct elesiver	https://doi.org/10.1016/j.jcis.2021.11.074	https://doi.org/10.1016/j.jcis.2021.11.074	Yes
7	Binder-Free Synthesis of Mesoporous Nickel Tungstate for Aqueous Asymmetric Supercapacitor Applications: Effect of Film Thickness	Dilip J. Patil, Dhanaji B. Malavekar, Vaibhav C. Lokhande, Prity P. Bagwade, Sambhaji D. Khot, Taeksoo Ji, Chandrakant D. Lokhande	General Engineering	Energy Technology	2022	Science Direct elesiver	DOI: 10.1002/ente.202200295	DOI: 10.1002/ente.202200295	Yes
8	SILAR synthesized dysprosium selenide (Dy2Se3) thin films for hybrid electrochemical capacitors	S.D. Khot a, D.B. Malavekar a, R.P. Nikam a, S.B. Ubale a, P.P. Bagwade a, D.J. Patil a, V.C. Lokhande b, C.D. Lokhande	General Engineering	Synthetic metals	2022	Science Direct elesiver	https://doi.org/10.1016/j.synthmet.2022.117075	https://doi.org/10.1016/j.synthmet.2022.117075	Yes
9	Nanocrystalline cobalt tungstate thin films prepared by SILAR method for electrocatalytic oxygen evolution reaction	P.P. Bagwade, D.B. Malavekar, V. V. Magdum, S.D. Khot, R.P. Nikam, D.J. Patil, U.M. Patil, C.D. Lokhande	General Engineering	International Journal of Hydrogen Energy	2023	Science Direct elesiver	https://doi.org/10.1016/j.ijhydene.2022.11.090	https://doi.org/10.1016/j.ijhydene.2022.11.090	Yes
10	Analysis of Model based Shadow Detection and Removal in Color Images	Trupti Ghewari; S. R. Khot; M. D. Khatavkar	Electrical	Institute of Electrical and Electronics Engineers (IEEE)	2019	Institute of Electrical and Electronics Engineers (IEEE)	https://doi.org/10.1109/ICISC44355.2019.9036408	https://doi.org/10.1109/ICISC44355.2019.9036408	Yes

D. Y. PATIL TECHNICAL CAMPUS
Faculty of Engineering & Faculty of Management
Dist. Kolhapur
DTE Code 6780
TALSANDE

Director
D.Y. Patil Technical Campus
Faculty of Engineering & Faculty of Management
Talsande, Tal. Hatkanangale, Dist. Kolhapur

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RUBRICS

Development of Liquid-Liquid Extraction and Separation Method for Ruthenium(III) with 2-Octylaminopyridine from Succinate Media: Analysis of Catalysts[1]

V. J. Suryavanshi[a,b], M. M. Patil[a], S. B. Zanje[b], A. N. Kokare[b], A. P. Gaikwad[b], M. A. Anuse[b,*], and G. N. Mulik [a,]**

[a] *Department of Chemistry, Balwant College, Vita-415311, Maharashtra, India*

[b] *Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur-416004, Maharashtra, India*

**e-mail: maanuse@gmail.com*

***e-mail: ganpatraomulik@rediffmail.com*

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Abstract—Ruthenium(III) has been efficiently extracted from 0.05 M sodium succinate at pH 9.5 by 2-octylaminopyridine in xylene and stripped with aqueous 10% (w/v) thiourea solution and determined spectrophotometrically. Various parameters viz., pH, weak acid concentration, reagent concentration, stripping agents, contact time, loading capacity, aq. : org. volume ratio, solvent has been thoroughly investigated for quantitative extraction of ruthenium(III). The utility of method was analyzed by separating the ruthenium(III) from binary mixture along with the base metals like Cu(II), Ag(I), Fe(II), Co(II), Bi(III), Zn(II), Ni(II), Se(II), Te(IV), Al(III) and Hg(II) as well as platinum group metals (PGMs). Ruthenium(III) was also separated from ternary mixtures like Os(VIII), Pd(II); Pd(II), Pt(IV); Pd(II), Au(III); Pd(II), Cu(II); Fe(II), Cu(II); Ni(II), Cu(II); Co(II), Ni(II); Se(IV), Te(IV); Rh(III), Pd(II); Fe(III), Os(VIII). The stoichiometry 1 : 2 : 1 (metal : succinate : extractant) of the proposed complex was determined by slope analysis method by plotting graph of $\mathrm{Log}\, D_{[\mathrm{Ru(III)}]}$ versus $\mathrm{Log}\, C_{[2\text{-OAP}]}$ and $\mathrm{Log}\, D_{[\mathrm{Ru(III)}]}$ versus $\mathrm{Log}\, C_{[\mathrm{succinate}]}$. The interference of various cations and anions has been studied in detail and the statistical evaluations of the experimental results are reported. The method was successfully applied for the analysis of ruthenium in various catalysts, synthetic mixtures corresponding to the composition of alloys and minerals.

Keywords: Solvent extraction, 2-Octylamiopyridine, Ruthenium(III), Sodium succinate, Catalysts, Alloys

DOI: 10.1134/S003602361702019X

INTRODUCTION

The recovery of strategic and precious metals from different matrices is always a challenging task for chemists. However, the scarcity of these metals had led to the need to recover them from low grade ores in which they are present in trace level. The great aesthetic value and technological importance of these metals has created never ending demand [1]. These metals have a wide range of industrial applications.

As one of the most effective hardeners in high-density alloys, Ruthenium is widely used in the electronic industry, medicine, for severe were resistance, raw material for catalyst and so on. It is also used to remove H_2S from oil refineries [2]. Ruthenium complexes are biologically important in detection of amino acids [3], iodine/iodide [4], vitamin A [5] and chlorophenaramine [6]. It acts as a versatile catalyst, used for removal of NO_x from air stream [7]. The isotope of ruthenium 106 used into radiotherapy of tumors, eyes and some ruthenium central complexes having properties of anticancer (http://education.Jlab.org/itselemental/ele044.html). The growing use of ruthenium in different field has made it necessary to develop simple, precise selective method for its separation as an analytical merit.

Solvent extraction is widely used for the separation of platinum group metals (PGMs) [8–12]. The extraction of ruthenium(III), Os(VIII) and Ir(III) was carried out by using Cyanex 921 [13] from an aqueous chloride media in toluene. The quantitative extraction of Ru(III) and Os(VIII) was observed within 0.01–0.05 M HCl concentration, beyond 1.0 M it gets decreased. The extractive separation of ruthenium(IV) in mineral acid medium (HCl) with N-octylaniline [14, 15] in xylene was also carried out. The quantitative extraction of ruthenium(IV) was observed in HCl and H_2SO_4, while $HClO_4$ and HBr medium showed incomplete extraction. The extraction of ruthenium(III) from a mixture of precious metal ions by

[1] The article is published in the original

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PAPER

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Liquid–liquid extraction and separation of lead(II) by using *N*-*n*-octylcyclohexylamine as an extractant: analysis of real samples†

Arjun Kokare, Vishal Suryavanshi, Sunil Zanje, Gurupad Kore and Mansing Anuse*

A method for the determination of micro amounts of lead(II) is described. *N*-*n*-Octylcyclohexylamine (*N*-*n*-OCA) was employed as an ion-pair forming a neutral [*N*-*n*-OCAH$^+$PbCl$_3^-$] complex in hydrochloric acid medium. The quantitative extraction of lead(II) was observed with *N*-*n*-OCA (0.03 to 0.055 M) in a dichloromethane (DCM) and xylene mixture (1 : 4), from hydrochloric acid medium (3.0 to 5.0 M). The extracted ion-pair complex was back stripped with 0.5 M nitric acid and determined spectrophotometrically with PAR. The quantitative extraction of lead(II) was found in the DCM : xylene ratio of 1 : 4 as a mixed solvent system. The various parameters studied, such as concentration of acid, *N*-*n*-OCA concentration, equilibrium time, solvent study, back stripping agents and loading capacity were optimized for the quantitative extraction of lead(II). The stoichiometry of the extracted ion-pair complex was determined on the basis of the slope analysis method, and it was found to be 1 : 3 : 1 (metal : chloride : extractant). The proposed method was successfully applied to the analysis of diverse ions, binary mixtures of associated metal ions, ternary mixtures, alloys, ayurvedic samples and water samples, by using *N*-*n*-OCA and lead(II) was determined using PAR and the results of analysis were confirmed by ICP-OES.

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1. Introduction

Nowadays, contamination of the environment by lead(II) and its compounds is a very important problem worldwide, due to its highly toxic, nonbiodegradable nature.[1] Lead(II) is a well known cumulative poison, found in the environment mostly because of mining and smelting, the manufacture of batteries, and its use as an additive. Concern about the toxicity of lead(II) has resulted in many substitutions in areas such as plumbing, painting, *etc.*[2] For many years, solvent extraction has been one of the most used techniques for the removal and separation of heavy metal ions at the pilot plant level, as well as in industrial skill processes. The general advantage of solvent extraction over the tridimensional method used as waste water treatment (chemical precipitation, coagulation–flocculation, ion-exchange, adsorption membrane filtrate) is the highly selective metal recovery from aqueous solution during continuous processes. It requires a low inventory of organic phase, low energy consumption, low capital operating cost, good selectivity and mass transfer in one step.[3] The efficiency of metal ion extraction depends on many parameters, such as ligand structure, solution acidity, type of solvent, temperature and time of process; however, the ability of the extractant to form metal ligand complexes has a crucial effect on the process selectivity.

Many extractants have been proposed for the separation and determination of lead(II) ions from various environmental samples (Table 1), including organophosphorus compounds,[4–9] microcyclic polyethers,[10] tetracarboxylresoric-*n*[4]arene,[11] calix[*n*]arene-based compounds[12–15] and high molecular weight amines[16–20] (Table 1).

In recent years we have explored some high molecular weight amines (HMWA), such as *N*-octylaniline,[16] *N*-*n*-octylaniline,[19] and 2-octylaminopyridine[20] for the extraction separation of lead(II) from acidic as well as alkaline medium. However, some cations and anions show interference in the extraction procedure of lead(II); extractions carried out in alkaline medium show interference from many ions,[16–18] and higher extractant concentration is required.[16,17,19]

In the present study, the authors have investigated the solvent extraction equilibria of lead(II) from aqueous hydrochloric acid solution, with a *N*-*n*-OCA mixture of DCM : xylene at room temperature, which minimises the interference of many cations and anions. The main purpose of the present work is to investigate the extraction mechanism in a hydrochloric acid medium. The hydrochloric acid medium was chosen as a convenient aqueous phase in which lead(II) could form an ion-pair complex with the secondary amine, and phase separation can take place very rapidly. It was observed that an increase in chloride concentration enhances the extraction, by the formation of the

Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur, 416 004, Maharashtra, India. E-mail: mansinganuse@yahoo.co.in

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Article

JOURNAL OF THE CHINESE CHEMICAL SOCIETY

Development of a Liquid-liquid Extraction System for Rhodium(III) by 2-octylaminopyridine from Weak Malonate Media

Vishal J. Suryavanshi,[a,b] Makrand M. Patil,[b] Arjun N. Kokare,[a] Sunil B. Zanje,[a] Rupali R. Pawar,[b] Mansing A. Anuse[a]* and Ganpatrao N. Mulik[b]*

[a]*Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University Kolhapur-416004, Maharashtra, India*
[b]*P. G. Department of Chemistry, Balwant College, Vita-415311, Maharashtra, India*

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We have developed the extraction method of rhodium(III) from malonate media with 2-octylaminopyridine (2-OAP) in xylene at pH 8.0. The quantitative extraction of rhodium(III) with extractant was found by screening of different physicochemical parameters like malonate concentration, extractant concentration, pH, diluents, effect of temperature, aq: org phase ratio, loading capacity of 2-OAP. The optimum condition was malonate = 0.025 M, pH = 8.0, 2-OAP = 0.05 M in xylene. The complete stripping of rhodium(III) from the loaded organic phase was carried out with 2 M HCl. Log-log plot was investigated to determine the stoichiometry of the extracted species and it was found to be 1:2:1 (metal:acid: extractant). The versatility of the proposed method was checked for extraction and separation of rhodium(III) from binary, ternary mixture of associated metal ions as well as platinum group metals and from the synthetic solution of rhodium minerals and alloys.

Keywords: Solvent extraction; 2-Octylamiopyridine; Rhodium(III); Sodium malonate; Minerals; Alloys.

INTRODUCTION

Solvent extraction of platinum group metals (PGM) has been extensively studied and always pursued to achieve their separation and purification.[1] Among the platinum group metals (PGMs) rhodium is one of the most expensive member and now a days it is indispensable for automobile catalytic converters. Such catalyst accessories contain platinum-group metals (PGMs), particularly platinum, palladium and rhodium, which play a key-role in the removal of pollutants from engine exhaust gas in locomotive vehicles. The recycling of PGMs contained in spent catalytic converters is a necessity not only due to their high economic value but also due to their potential environmental and health risks.[2] Rhodium is used as an alloying agent for hardening and improving the corrosion resistance of platinum and palladium. These alloys are used in furnace windings, bushings for glass fibre production, thermocouple elements, electrodes for aircraft spark plugs, and laboratory crucibles. It is used as an electrical contact material due to its low electrical resistance, low and stable contact resistance, and its high corrosion resistance.[3] Rhodium has a wide range of applications in the production of alloys, optical instruments and jewellery as well as it is used in electronic devices, catalytic reactions and space materials. Recently, it has been employed in automobile catalytic converters as a monitor to control NOx emission.[4] Rhodium has low abundance, high price and wide range of applications; hence the development of an innovative method for its separation would be of analytical merit.

The industrial extraction of rhodium is complex as the metal occurs in ores mixed with other metals such as palladium, silver, platinum, and gold. It is found in platinum ores and obtained free as a white inert metal which is very difficult to fuse. The annual world production of this element is only about 25 tons and there are very few rhodium minerals. The high prices of precious metals like platinum group metals (PGMs) have ensured that there is continued interest in the development of new extractants for the commercial concentration and separation of these metals.

The availability of PGMs in old scrap contributes great economy of PGM usage and technological importance of these metals has created a never ending demand.[5] The recovery of these precious metals such as Pt and Rh from different matrices is always a challenging task for the chemists and their recycling is of economical importance.[6] Solvent extraction (SX) and ion exchange (Amberlite

* Corresponding author. Tel: 02347-272096; Email: ganpatraomulik@rediffmail.com

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PHYSICAL CHEMISTRY OF SOLUTIONS

Development of a Rapid and Reliable Liquid-Liquid Extractive Method for the Effective Removal of Chromium(VI) from Electroplating Waste Water and Tannery Effluents[1]

Arjun Kokare, Vishal Suryavanshi, Sunil Zanje, Gurupad Kore, Dhuryodhan Waghmode, and Mansing Anuse *

Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur, Maharashtra, 416004 India

**e-mail: maanuse@gmail.com, mansinganuse@yahoo.co.in*

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Abstract—A rapid and selective liquid-liquid extractive system is developed for extraction of Cr(VI) by employing N-*n*-OCA reagent and xylene as solvent. Quantitative extraction of Cr(VI) is observed in the concentration range of 0.4 to 0.7 M HCl. The extracted [Cr(VI)-N-*n*-OCA] complex from the organic phase was back extracted by 6.0 M ammonia (3 × 10 mL) and spectrophotometrically quantified. Various parameters were explored to study their influence on quantitative extraction of Cr(VI) by varying N-*n*-OCA concentration, equilibration time, effect of diluents, acid concentration and diverse ions. Stoichiometry of the extracted complex showed 1 : 1 ratio of acid and amine. The relative standard deviation of the developed method is 0.09 with respect to calibration range 0.2 to 0.8 μg mL^{-1}. The validity of the proposed method was checked by applying it to the associated and toxic metals in binary, synthetic mixtures and ternary effluents.

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INTRODUCTION

The abundance of chromium in earth crust is 0.014% [1] and is among the most valuable element considering its wide variety of applications in industries like electroplating, metal finishing processes [2], dyes, pigments, tannery industries etc [3]. However, on the other hand the impact of Cr(VI) on pollution is increasing day by day and the toxicity of chromium compounds is known to depends upon on its oxidation states [4]. Chromium(III) is relatively less toxic where as Cr(VI) has high potential for toxicity. Human toxicity includes lung as well as kidney cancer, liver and gastro-intestinal damage. This is the reason why exposure to Cr(VI) has been recognized as potential hazardous by national and international organizations around the globe. The International Agency for Research on Cancer (IARC) has classified Cr(VI) in group I as a human carcinogen [5]. The permissible exposure limits in the air for Cr(VI) is 5 mg m^{-3} [6]. Hence, it is highly important to address the issue pertaining to effective removal of total chromium present in these environmental effluents.

There is extensive literature demonstrating advanced methods for the removal of chromium from various samples [7–16]. Recently, special materials like nonporous silica [17], thermoresponsive polymeric resin [18], Dowex M4195 chelating resin [19], hybrid inorganic-organic adsorbents 20, functionalized pyridine copolymer with amine groups [21], etc has been explored with great interest and proved to be excellent in the removal of chromium(VI). However, liquid-liquid extraction being a simple and versatile technique in hydrometallurgy, it is relatively less explored. Employing chelating or complexing agents has been one of the versatile approach where long chain amine have been proven to be good extractant for the removal of chromium(VI) [22–31]. In these studies the yield of extraction, concentration of extractant, equilibrium time, stripping study and their recoveries have been evaluated by quaternary ammonium salts such as trioctyl methyl ammonium compounds, aliquot 336 [22], alamine 336 [23], Amberlite LA1 and LA2 in MIBK24, tri-*n*-dodecylamine [25], tribenzylamine [26], trioctyl ammonium chloride [27], aliquot 336 with membrane [28] and packed polystyrene microcapsules [29], DTHP [30] and TBP [31].

The present study reports an effective extractive approach for the removal of Cr(VI) using a long-chain amine N-*n*-octylcyclohexylamine (N-*n*-OCA). N-*n*-octylcyclohexylamine can be easily synthesized from cyclohexylamine and acetonitrile without any other impurities (i.e. 100% yield) and recovery of extractant is possible after extraction of metal. Hence, N-*n*octylcyclohexylamine is explored as extractant for the removal of Cr(VI). The aim of this study is to suc-

[1] The article is published in the original.

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cogent chemistry

ANALYTICAL CHEMISTRY | RESEARCH ARTICLE

Solvent extraction studies of rhodium(III) by using *n*-octylaniline from malonate media: Analysis of synthetic mixtures and alloys

Ashwini P. Gaikwad[1], Vishal J. Suryavanshi[1] and Mansing A. Anuse[1]*

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*Corresponding author: Mansing A. Anuse, Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur 416004, India
E-mail: maanuse@gmail.com

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Marcus Vinicius Tres, Universidade Federal de Santa Maria, Brazil

Additional information is available at the end of the article

Abstract: Herein, we have developed the solvent extraction method for the selective separation of precious rhodium(III). Various physicochemical parameters like pH, malonate concentration, *n*-octylaniline concentration, equilibrium time, aq: org phase ratio, and loading capacity of *n*-octylaniline are optimized for the quantitative recovery of the rhodium(III). The composition of the extracted species was determined by plotting the log–log graph of Log $D_{[Rh(III)]}$ vs. Log $C_{[n\text{-octylaniline}]}$ and Log $D_{[Rh(III)]}$ vs. Log $C_{[malonate]}$; the stoichiometry was found to be (metal: acid: extractant) 1:2:1. The proposed method was successfully applied for the separation of rhodium(III) from various binary and ternary mixtures of associated metal ions. The separation of the rhodium(III) from real samples was also carried out with the proposed method. The proposed method was applied for analysis of synthetic mixture corresponding to alloys such as pseudo-palladium, iron–rhodium alloy, platinum–rhodium alloy, and rhodium–platinum catalyst.

Subjects: Separation Processing; Ion Exchange; Solvent Extraction

Keywords: solvent extraction; rhodium(III); sodium malonate; *n*-octylaniline; synthetic mixtures and alloys; pH

1. Introduction

At present, there is a growing demand for platinum group metals; the name platinum group metals (PGMs) includes six elements: ruthenium, rhodium, platinum, palladium, osmium, and iridium. In the past few decades, these metals have found new applications in the jewellery and decorative

Mansing A. Anuse

ABOUT THE AUTHORS

My research group is mainly involved in the development of easier and cost-effective liquid–liquid extraction technique for the separation and determination of various metal ions with high molecular weight amines. The applicability of the developed method was investigated for the analysis of alloys, minerals, waste water, synthetic mixtures, ayurvedic samples, etc. The group is also occupied in the synthesis of complexing reagent for the invention of spectrophotometric determination method. The research interest is the intention of achieving eco-friendly method to reduce the consumption of chemicals, cost, and time.

PUBLIC INTEREST STATEMENT

Rhodium is one of the most abundant elements of platinum group metals. The cost of this metal is very high and applications are very tremendous. It is used in the catalytic converter for changing risky unburned hydrocarbons, carbon monoxide, and nitrogen oxide exhaust emission into fewer noxious gases; it is also used as a catalyst in electroplating. Though its sources are limited over its deployment, its separation is most important. In this article, we used liquid–liquid extraction based on high molecular weight amine such as *n*-octylaniline. The percentage of extracted rhodium was determined spectrophotometrically. The selectivity, extractant concentration, influence of weak organic acid, phase ratio, extractant, binary mixture separation, and analysis of alloys were also considered in this study.

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CHEMISTRY & BIOLOGY INTERFACE

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Selective liquid-liquid extraction and separation of palladium(II) from salicylate media with *n*-octylaniline in xylene: analysis of catalyst, alloys

Ashwini Gaikwad[1], Vishal Suryavanshi[1], Mansing Anuse[1]

[1]*Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur 415311*
**E-mail: maanuse@gmail.com*
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Abstract: Solvent extraction method for separation of palladium(II) was developed from salicylate medium. The optimized extraction condition of palladium(II) was successfully utilized for the separation of palladium(II) from its various binary and ternary mixtures of associated metal ions. The effect of temperature on palladium(II) extraction was investigated. The stoichiometry of the extracted species of palladium(II) - salicylate was determined from log-log plot and it is observed as 1:3:1. The applicability of the proposed method was checked by analyzing various catalyst and alloy samples.

Keywords: Liquid-liquid extraction, Palladium(II), Sodium salicylate, *n*-Octylaniline, Alloys and catalyst

1. Introduction

Solvent extraction has attracted much attention as an effective and energy saving category of separation technique for precious metals. The extraction technique is one of the most important process for the recovery of precious metals from waste water and scraps as well as in the mining industry. At present, there is a growing demand of precious metals for technological applications due to their outstanding physical and chemical properties [1]. The abundance of palladium in the earth's crust is 0.01-0.02 μg mL^{-1} and it exists in various natural minerals, soils and rocks [2]. This element is of immense importance to the electronic industries [3]. Palladium and its alloys have a wide range of applications both in the chemical industry and in instrument making. It also has widespread use in dental and medicinal devices and jewellery manufacture [4]. The carcinogenicity of palladium(II) compounds in rats and mice and their toxicity to mammals, fish and higher plants are cause for environmental concern [5]. Therefore, these compounds are usually considered as environmental pollutants [6]. Palladium(II) forms a number of complexes that are soluble in organic solvents because

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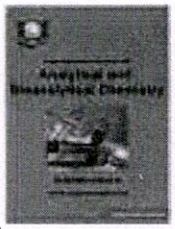

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Original Article

Liquid-liquid extraction of iridium(III) from malonate media using liquid anion exchanger

Ashwini Gaikwad, Swapnil Jagatap, Vishal Suryavanshi, Sanjay Kolekar, Mansing Anuse*.

Affiliation:- Analytical Research Laboratory, Department of Chemistry,
Shivaji University, Kolhapur. India – 416004
Email id: - mansinganuse@yahoo.co.in.

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Abstract

A new analytical procedure for the separation of Iridium(III) from platinum group metals presented here. A systematic study of solvent extraction behavior of Iridium(III) with n-octylaniline from malonate media was carried out. Iridium(III) was quantitatively extracted from 0.050 – 0.065 M sodium malonate at pH 7.0-8.5 with 0.2 M n-octylaniline in toluene. The extraction was found to proceed by an anion exchange mechanism with the extraction species being $[CH_3(CH_2)_7C_6H_4NH_3^+\ Ir(C_3H_2O_4)^-_2]_{org}$ ascertained on the basis of slope analysis. The extracted metal ion was separated by selective stripping with hydrochloric acid from the metal loading organic phase and estimated spectrophotometrically. A binary separation of Iridium (III) from Pt(IV), Pd(II), Ru(III), Au(III), Os(VIII), Se(IV), Te(IV), Fe(III),Co(II), Ni(II) and Cu(II) is discussed. Applicability of the process is studied by the separation of Iridium(III) from ternary mixtures.

Introduction

The recovery of platinum group metals (PGMs) such as Ir, Ru, and Rh from different matrices is always a challenging task for a chemist. The great aesthetic value and technological importance of these metals has created a never-ending demand [1]. These metals are scarce and have a wide range of industrial applications. The determination of iridium has always been difficult. The extremely inert character of iridium complexes creates a most challenging problem in their separation. Recovery of iridium from spent catalysts and recycling is economically important [2, 3]. In the recycling industry, there are three main categories of refining materials. Primary materials such as gold-/silver ore and PGM concentrates come directly from the mining industry. The most important category, secondary materials, includes chemical/petrochemical catalysts, automotive catalysts, and sweeps or bullion-type material from numerous industrial applications. A third category of growing importance is called "tertiary material" and consists of waste from other precious-metal refining plants, such as insoluble from wet chemical operations, PGM sweeps from Ag/Au refiners, and Ir-/Ru-/ Rh-concentrates [4].

Several extraction methods have been developed for iridium [5-8]. The extraction of Iridium(III) from similar extraction behavior of rhodium(III) and hydrochloric acid and hydrobromic acid 5 % tri-iso-octylamine solution in carbon tetrachloride has been studied [9]. A liquid-liquid extraction of Iridium(IV) from chloride solution was studied under different condition of aqueous and organic phase compounds concentration using alamine-336 [10-14] as an extractant. The extraction of iridium from its chloride solution was carried out using commercially available solvent extraction reagents alamine 300 [14] and aliquat 336 [14,15]. Liquid-liquid extraction of Iridium(III) and separation of it from other platinum group metals (PGM) from Cl_2/HCl leaching of the ores or concentrations converted into thiourea eluate resin were studied, with high molecular weight tertiary amines as extractants [16]. A new method for the separation and spectrophotometric analysis of iridium by biphasic extraction system of n-propyl alcohol-sodium chloride – water [17] was studied. The method was used for the determination of iridium from Pt-Pd-Ir alloy samples. pH effect was studied on solvent extraction of Iridium(III) sulfates with N-octyl-, N,N-dioctyl aniline and N,N,N-trioctyl anilinium O,O-di(iso-propyl)dithiophosphates [18]. Solvent extraction behavior of Iridium(III) with salicylhydroxamic acid (SHA) [19] in isobutanol from aqueous chloride solution was studied and compared with

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Liquid–liquid extraction of thorium(IV) with *N*-*n*-heptylaniline from acid media

Rupali R. Pawar[1] · Vishal J. Suryavanshi[1] · Suresh T. Salunkhe[1] · Suresh S. Patil[2] · Ganpatrao N. Mulik[1]

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Abstract The extraction behavior of thorium(IV) from sulphuric acid medium with *N*-*n*-heptylaniline in xylene. Various parameters like reagent concentration, acid concentration, equilibration time, diverse ions and effect of diluents were studied. Thorium(IV) was selectively extracted and separated from many metal ions. The nature of the extracted species was determined. Thorium(IV) was analyzed from monazite ore and gas mantle.

Keywords Thorium(IV) · Liquid–liquid extraction · H_2SO_4 · *N*-*n*-Heptylaniline

Introduction

Thorium is a naturally occurring, radioactive metal. Nowadays thorium is used in nuclear power generation. So it is the need of time that it should be extracted and finally in pure form. Vary many amines have been used for the extraction of thorium(IV) like Amberlite LA-1 or LA-2 [1], *N*-*n*-octylaniline [2], mixture of *N*-*n*-octylaniline and trioctylamine [3], 2-octylaminopyridine [4] and various extractants like di-(2-ethylhexyl) 2-ethylhexyl phosphonate [5], bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) [6], organo phosphoric compounds from various media [7–15], TODGA in ionic liquids have been successfully employed for the recovery of thorium(IV) in industry [16]. Extraction of uranium(VI) and thorium(IV) by triphenylarsine oxide from salicylate media has been carried out [17]. Liquid–liquid extraction of uranium(VI) and thorium(IV) by two open-chain crown ethers with two terminal quinolyl groups in chloroform were studied [18].

Extraction of uranium(VI), zirconium(IV) and thorium(IV) by PC-88A from perchlorate media have been carried out [19]. Extraction of thorium(IV) from nitrate solution by bis-2-(butoxyethylether) was reported [20]. The extraction studies of uranium(VI) and thorium(IV) with TBPO in toluene from sodium salicylate medium were studied [21]. The extractive separation of thorium(IV) and praseodymium(III) with Cyanex 301 and Cyanex 302 from nitrate medium were studied [22]. The extraction behaviors of uranium(VI), thorium(IV) and lanthanides were studied using Cyanex 923 in toluene from different mineral acid media [23]. Further, high molecular weight amines are also used for the extraction and determination of a variety of other metal ions [24–26].

Previously we have reported the solvent extraction methods for the quantitative extraction of platinum group metals with amines [27–30]. In the present study extraction behavior of thorium(IV) from sulphuric acid media by *N*-*n*-heptylaniline is undertaken. Various parameters such as reagent concentration, acid concentration, effect of diluents, phase ratio, shaking period, loading capacity and diverse ions were studied. Separation of thorium(IV) from binary as well as multicomponent mixtures was achieved and also from associated elements in geological and real samples. The proposed method is relatively simple, rapid and selective used for the separation from many metal ions successfully.

✉ Ganpatrao N. Mulik
ganpatraomulik@rediffmail.com

[1] P.G. Department of Chemistry, Balwant College, Vita 415311, India

[2] P.G. Department of Chemistry, PDVP College, Tasgaon 416312, India

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Development of novel solvent extraction method for determination of gold(III) using 4-heptylaminopyridine: Application to alloys and environmental analysis

Balaji T. Khogare[a,b,*], Ganesh S. Kamble[c], Arjun N. Kokare[c], Sunil B. Zanje[c], Vishal J. Suryavanshi[c], Mansing A. Anuse[c], Pravina B. Piste[b,**], Balasaheb N. Kokare[a,**]

[a] Department of Chemistry, Raje Ramrao Mahavidyalaya, Jath Dist-Sangli-416404, (M.S), India
[b] P.G. Department of Chemistry, Yashwantrao Chavan Institute of Science, Satara-415001,(M.S), India
[c] Analytical Chemistry Research laboratory, Department of Chemistry, Shivaji University Kolhapur-416004, (M.S), India

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ABSTRACT

In this paper, the solvent extraction of gold(III) from malonate media (0.04 mol L^{-1}) has been studied by equilibrating aqueous phase having pH 2.5 with 10 mL of 0.07 mol L^{-1} 4-heptylaminopyridine (4-HAP) as a novel anion exchanger diluted in xylene for 2 min. The extracted metal from organic phase was separated by stripping with 5.0 mol L^{-1} NH_3 solution (2 × 10 mL). The effect of various parameters, such as pH, extractant concentration, weak acid concentration, equilibrium time, stripping agents, aqueous to organic volume ratio and diluents on the extraction of gold(III) was investigated. The extracted species has been evaluated from $\log D$ vs $\log C$ and species appears to be 1:2:1 (metal: acid: extractant). The selectivity of the method was checked by separating gold(III) from binary and ternary mixtures of associated metal ions as well as platinum group metals(PGMs). The separation of gold(III) from synthetic alloys and environmental samples was also carried out.

1. Introduction

Gold is one of most important nobel metals due to its wide applications in industrial and economic activities. The most common uses of gold are in the industry of jewelry and electronics [1]. On the other hand, some of the gold(I) compounds have biological activity, which are employed in medicine as anti-inflammatory drugs in the treatment of rheumatoid arthritis [2]. Nowadays, the consumption of gold has increased and therefore, the cost of gold production and its price in the market have risen rapidly. However, some wastes such as the waste of electronic equipment (e-waste) contain large amounts of precious metals compared to their own respective ores and, therefore, such wastes may be considered as a secondary source of valuable metals [3]. There is great interest in the removal and recovery of gold metals from wastewater. The two most important reasons and motivations for gold metals removal are the economical impact of losing these metals and their environmental concerns [4]. Trace amounts of these gold metals can be found in some wastewaters as a result of mining [5], electroplating industries [6], or electronic and Jewellery manufacturing. Hence, the development of low cost, and selective technologies for gold ion uptake from industrial effluents is extremely important from economic and environmental points of view, because the recovered ions can be converted into elemental gold.

Many techniques are available for the determination of gold ions from aqueous solutions, such as inductively coupled plasma mass spectrometry (ICP-MS) [7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8], electrochemical [9], neutron activation analysis [10] and atomic absorption spectrophotometry (AAS) [11]. Some factors such as the initial cost of instruments, technical know-how, consumable and costly maintenance of technique restrict the wider applicability of these techniques, particularly in laboratories with limited budgets in developing countries. Solvent extraction has been considered to be a promising technology for recovery and separation of gold with the advantages of high efficiency and simple operation [12,13]. In recent years, some papers have been published on gold(III) extraction using various extractants such as 4-(4-methoxybenzylideneinino)-5-methyl-4H-

* Corresponding author at: Department of Chemistry, Raje Ramrao Mahavidyalaya, Jath Dist-Sangli-416404, (M.S), India.
** Corresponding authors.
E-mail addresses: khogare1988@rediffmail.com (B.T. Khogare), ppiste321@gmail.com (P.B. Piste), bnkokare@rediffmail.com (B.N. Kokare).

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Liquid- Liquid Extraction of Zinc(II) From Acid Media with N-n-Heptylaniline as an Extractant: Analysis of Pharmaceutical and Commercial Sample

Pawar RR[1], Suryavanshi VJ[1], Patil MM[1], Patil SS[2] and Mulik GN*[1]

[1]*Department of Chemistry, Balwant College, Vita-415311, India*

[2]*Department of Chemistry, PDVP College, Tasgaon-416312, India*

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***Corresponding author:** Mulik GN, P.G. Department of Chemistry, Balwant College, Vita-415 311, India

Abstract

The extraction of zinc(II) from acid media by N-n-heptylaniline in xylene has been studied for metal distribution measurements. Various physicochemical parameters like acid concentration, reagent concentration, equilibrium time, effect of diluents, aqueous to organic phase ratio, stripping agents and loading capacity were investigated for the quantitative extraction. The extraction was carried out from 3 M hydrochloric acid and 0.5 M N-n-heptylaniline concentration. Zinc(II) was selectively extracted and separated from many metal ions and synthetic mixtures. The nature of the extracted species was determined. Zinc(II) was analyzed from pharmaceutical samples and nycil talk powder.

Keywords: Zinc(II); Liquid-Liquid Extraction; Acid Media; N-n-Heptylaniline; Pharmaceutical Samples; Nycil Talk Powder

Introduction

The uses of zinc(II) are in the production of die-casting alloys, in galvanizing industry, pharmaceutical samples, in the manufacture of brass products, rolled zinc(II) products of various types, light metal alloys, in desilvering lead and in wet-batteries. It is starting material for the production of zinc(II) oxide. Zinc(II) is an essential trace element in plant and animal life. The zinc(II) content in humans is 2 - 4g [1]. Zinc(II) is also essential constituent of several enzymes necessary for metabolism. It is necessary to develop the simple, rapid and selective method of separation for zinc(II) from different elements. For extraction and separation of zinc(II) solvent extraction is useful method. Solvent extraction of zinc(II), indium(III), thallium(III) and bismuth(III) with n-octylaniline from hydrochloric acid media and their separation carried out [2].

The distribution equilibrium of zinc(II) between synergistic mixture of N-n-octylaniline and trioctylamine in xylene from thiocyanate media has been investigated [3]. The solvent extraction of zinc(II) from thiocyanate and sulphuric acid media using N-n-hexylaniline in xylene is described [4]. Solvent extraction of zinc from strong hydrochloric acid solution with alamine 336 has been carried out [5]. Liquid-liquid extraction of zinc(II) by 3-methyl-quinoxaline-2-thione from nitrate medium investigated [6]. Separation of iron and zinc(II) from manganese nodule leach liquor using TBP as extractant is studied [7]. Solvent extraction utilized for the selective separation of zinc(II) from other elements in hydrometallurgical processing of resources [8]. Zinc(II) chloride and hydrochloric acid extraction from solutions of high zinc(II) concentration by tri-n-butyl phosphate diluted in ShellSol2046 (an aliphatic solvent) has been studied with a combination of experiments and mathematical Modeling [9]. From chloride solutions solvent extraction of zinc(II) carried out [10].

The mean centering of ratio kinetic profiles method was used for the simultaneous determination of binary mixtures of Ni(II) and Zn(II) in water samples, without prior separation steps [11]. Synergistic extraction of zinc(II) by mixtures of primary amine N1923 and cyanex 272 investigated [12]. The solvent extraction of zinc(II), cadmium(II) and chromium(III) from phosphoric acid solutions by tri-n-butyl phosphate in kerosene as diluent was investigated [13]. The extraction and separation of zinc(II), manganese(II), cobalt(II) and nickel(II) from nickel laterite bacteria leach liquor were carried out using sodium salts of TOPS-99 and Cyanex 272 in kerosene [14]. The selective removal of zinc(II) over iron (II) by liquid-liquid extraction from spent hydrochloric acid pickling effluents produced by the zinc(II) hot-dip galvanizing industry was studied at room temperature [15]. Extraction and separation of cobalt(II) and zinc(II) was studied from a sulphate solution using Na-D2EHPA, NaPC88A and NaCyanex 271 of 0.04M concentration [16]. The liquid-liquid extraction of zinc(II) using D2EHPA as extractant has been investigated in order to recover

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Liquid-liquid extraction studies of ruthenium(III) from malonate medium using *n*-octylaniline as an ion-pairing reagent: study of catalyst and alloys

A. P. Gaikwad, V. J. Suryavanshi, M. A. Anuse*

Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur-416004, Maharashtra, India

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Herein we have developed a solvent extraction system for ruthenium(III) by using 0.1 M *n*-octylaniline in 0.05 M malonate medium at pH 3.5. Various operational parameters like pH, reagent concentration, weak organic acid, equilibrium time, and loading capacity of extractant were optimized for the quantitative recovery of ruthenium(III). Stoichiometry of the extracted species was resolved by the slope ratio analysis method. The extraction takes place by formation of an ion-pair complex between the $[CH_3(CH_2)_7C_6H_4NH_3]^+_{(org)}$ species and the $[Ru(C_3H_2O_4)_2]^-_{(aq)}$ species. The association of these two species yielded the uncharged neutral extractable species $[CH_3(CH_2)_7C_6H_4NH_3^+ Ru(C_3H_2O_4)^-_2]_{(org)}$. The stoichiometry of the extracted species was found to be 1: 2: 1 (metal: acid: extractant). The soundness of the proposed method was checked by extracting ruthenium(III) from binary and ternary mixtures and various catalysts were also investigated.

Keywords: Liquid-liquid extraction, *n*-Octylaniline, Ruthenium(III), Sodium malonate, Catalyst.

INTRODUCTION

Ruthenium is a very rare element that is found about 10^{-8} % on earth's crust. Chondrite and especially iron meteorites contain high amounts of ruthenium ($1\text{-}6 \times 10^{-4}$ %). Ruthenium also occurs in alliance with other platinum group metals [1]. Ruthenium is a rare polyvalent hard white transition metal. Small amount of ruthenium can impart hardness to platinum and palladium. The resistivity to corrosion of titanium was noticeably increased by a small amount of ruthenium [2]. Ruthenium is a versatile catalyst. It is used to remove H_2S from oil in oil refineries [3]. The use of ruthenium is compatible with semiconductor processing techniques; therefore, it is used as a material for microelectronics [4]. Ruthenium is very hard and corrosion resistant, therefore it is used for coating of electrodes by the chloralkali process, the outcome of the process gives chlorine and caustic soda which are applicable for a wide range of industrial and domestic applications. The application of ruthenium in alloys of aircraft turbine blades will reduce the CO_2 impact of air travel on the environment in the future. If present prototypes are doing well, its high temperature stability and high melting point will permit elevated temperatures and thus more efficient burning of aircraft fuel [5]. Recently, platinum group metals (PGMs), particularly ruthenium and its chlorocomplexes, have been largely used for the catalytic oxidation of organic compounds. Organometallic ruthenium carbene and allenylidene complexes are efficient catalysts for olefin metathesis [6]. Generally, ruthenium complexes have better resistance to hydrolysis and have more choosy action on tumors. Ruthenium and its alloys have a well-known application in jewelry [1]. The increasing applications of ruthenium in various fields have made it compulsory to develop a simple, inexpensive and sensitive method for its separation and determination.

In current days a variety of reagents have been considered for liquid-liquid extraction of ruthenium(III). 2-Mercaptobenzimidazole is used as extractant for ruthenium(III) in n-butanol [7]; 3-hydroxy-2-methyl-1-phenyl-4-pyridone [8], Cyanex 921 [9], Cyanex 923, Cyanex 471, Cyanex 272, LIX 54, LIX860N-I [10] are reported for solvent extraction. Bis (2-ethylhexyl) phosphoric acid [11, 12] and tributylphosphate [13] extract the nitrosyl-ruthenium complex in dodecane. Solvent extractions using high molecular weight amines (HMWA) turn more and more popular in modern years. The HMWA are well-known as liquid anion exchangers, which combine several advantages of liquid-liquid extraction and ion exchange. High molecular weight amines (HMWA) reported for ruthenium(III) extraction are: Alamine 336 [14], Alamine 300, Aliquat 336 [10], N-octylamine [15]. Extraction of ruthenium from HCl media has been performed with N,N'-dimethyl-N,N'-dicyclo-hexylmalonamide (DMDCHMA) dissolved in 1,2-dichloroethane [16]. Alkylaniline hydrochloride [17] extracts ruthenium from chloride or sulfate medium into toluene. The oxygenated and hydrocarbon solvents like methyl isobutyl ketone

* To whom all correspondence should be sent:
E-mail: maanuse@gmail.com

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ARTICLES

2-nitrobenzaldehyde Thiocarbohydrazone Assisted Precise Extraction Spectrophotometric Method for the Determination of Ruthenium(III) in Alloy and Catalysts[1]

Sunil B. Zanje, Vishal J. Suryavanshi, Arjun N. Kokare, Anita A. Ghare, Ganesh S. Kamble, Pravin N. Kamble , and Mansing A. Anuse*

Analytical Chemistry Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur, 416004 India

**e-mail: maanuse@gmail.com*

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Abstract—A simple, rapid, selective, sensitive and reliable extractive spectrophotometric method was developed for the determination of ruthenium(III) using 2-nitrobenzaldehyde thiocarbohydrazone (**2-NBATCH**) as a chromogenic chelating ligand. The ruthenium(III)–2-NBATCH complex is formed in aqueous acetic acid media (0.7 M) containing an organic solvent after 5 min heating on a water bath. The red colored complex is extracted into 1,2-dichloroethane and absorbance is measured at 445 nm against reagent blank. The Beer's law is obeyed within 1–6 g/ mL of ruthenium(III), the optimum concentration range was 2–5 g/ mL of ruthenium(III) evaluated by Ringbom's plot. Molar absorptivity and Sandell's sensitivity of complex were 1.41×10^4 L/ mol/cm and 0.0075 μg/cm^2, respectively. The stoichiometry of complex was 1 : 3 established from Job's method of continuous variation, molar ratio method and logarithmic slope method. The proposed method was applied for determination of ruthenium(III) in binary and ternary, synthetic mixtures corresponding to fission product elements alloy and ruthenium(III) catalysts.

Keywords: ruthenium(III), 2-nitrobenzaldehydethiocarbohydrazone, extractive spectrophotometry

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Ruthenium is a scarce element found in the metallic state associated with other platinum group metals and coinage metals. Its abundance is 0.0001 ppm by weight in the earth's crust [1]. Ruthenium is present in such minerals as laureate, ruteniridosmine and ruthenosmiridium as well as chondrites and iron meteorites (10^{-4}%) [2]. Ruthenium and its alloys are of commercial importance as they have wide applications in jewelry because of high resistance to chemical attack and stable electrical properties. Ruthenium is most effective hardener in high density alloys, it is widely used in electronic industries, it also acts as a versatile catalyst used for removal of NO_x from air stream [3]. Ruthenium compounds are also used as anticancer drug [4] and for identification of amino acids [5], iodine/iodide [6], vitamins A [7] and chlorophenaramine [8]. Some ruthenium complexes are used for light absorption in dye-sensitized solar cells [9].

The all-round use of ruthenium in various fields very well justifies the scope for the development of low cost, selective, sensitive and precise methods for its determination. There are many sensitive, but expensive analytical methods such as electrocatalytic voltammetry [10], spectrofluorimetry [11], electrochemiluminiscence [12], catalytic spectrophotometry. [13], flow injection catalytic spectrophotometry [14], electrothermal atomic absorption spectrometry [15] and graphite furnace atomic absorption spectrometry [16], inductively coupled plasma atomic emission spectrometry [17], inductively coupled plasma-optical emission spectrometry [18] and inductively coupled plasma mass spectrometry [19]. However, these instrumental techniques involve many complicated processing steps and serious interferences from other metal ions. On the other hand, spectrophotometric method still has the advantage of simplicity and does not need expensive or complicated equipment.

A number of methods were developed for the determination of ruthenium(III) using chromogenic reagents among them thiourea [20], and derivatives [21, 22]. Determination using thiourea is sensitive and easily practicable but suffers from many drawbacks, viz. higher hydrochloric acid concentration (6 M), 10 min heating or one hour standing time and interference of other platinum group metals. Another chromogenic reagents are such as 1,3-bis(hydroxymethyl)benzimidazole-2-thione [23], *o*-methylphenyl thiourea [24], isoamyl xanthate [25], 5-

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Development of a reliable analytical method for the precise extractive spectrophotometric determination of osmium(VIII) with 2-nitrobenzaldehydethiocarbohydrazone: Analysis of alloys and real sample

Sunil B. Zanje [a], Arjun N. Kokare [a], Vishal J. Suryavanshi [a], Duryodhan P. Waghmode [a], Sunil S. Joshi [b], Mansing A. Anuse [a,*]

[a] Analytical Chemistry Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur 416004, India
[b] Department of Humanities and Basic Sciences, TKIET, Warananagar, Kolhapur, Maharashtra, India

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ABSTRACT

The proposed method demonstrates that the osmium(VIII) forms complex with 2-NBATCH from 0.8 mol L^{-1} HCl at room temperature. The complex formed was extracted in 10 mL of chloroform with a 5 min equilibration time. The absorbance of the red colored complex was measured at 440 nm against the reagent blank. The Beer's law was obeyed in the range of 5–25 μg mL^{-1}, the optimum concentration range was 10–20 μg mL^{-1} of osmium(VIII) as evaluated by Ringbom's plot. Molar absorptivity and Sandell's sensitivity of osmium(VIII)-2NBATCH complex in chloroform is 8.94×10^3 L mol^{-1} cm^{-1} and 0.021 μg cm^{-2}, respectively. The composition of osmium(VIII)-2NBATCH complex was 1:2 investigated from Job's method of continuous variation, Mole ratio method and slope ratio method. The interference of diverse ions was studied and masking agents were used wherever necessary. The present method was successfully applied for determination of osmium(VIII) from binary, ternary and synthetic mixtures corresponding to alloys and real samples. The validity of the method was confirmed by finding the relative standard deviation for five determinations which was 0.29%.

1. Introduction

Osmium is a very rare in nature, it is found in the metallic state together with the platinum group metals (PGMs) and the coinage metals. Its abundance in the earth's crust is 0.005 ppm by weight [1]. Osmium is frequently used in small quantities in alloys where frictional wear must be minimized. These alloys are typically used in ballpoint pen tips, fountain pen tips, record player needles, electrical contacts, high pressure bearings, implants such as pacemakers and replacement valves [2]. This alloy predominantly used because its resistance to corrosion. The use of osmium tetroxide in biological processes such as fixatives for the preservation of biological tissue and its delineation for optical and electronic microscopy [3]. Osmium tetroxide is used for fingerprint detection [4]. Osmium complexes have recently been used as potential anticancer drugs [5,6], treatment of arthritic joints [7]. Osmium is used an ultra-incompressible, hard material viz. abrasives, cutting tools and coatings where wear prevention [8]. Osmium tetroxide is an efficient catalyst for dihydroxylation of olefins [9]. The osmium polymer mediated biosensor is used for the determination of fructose [10]. Wide range of applications of osmium increased the demand. Therefore the analytical point of view, there is a necessity to develop a sensitive, selective, highly precise and economical method for its quantitative determination.

There are many sensitive, but expensive analytical methods for the determination of osmium viz. catalytic kinetic spectrofluorimetry [11], catalytic kinetic determination [12], flow injection kinetic spectrofluorimetric determination [13], graphite furnace atomic absorption spectrometry [14], inductively coupled plasma mass spectrometry [15], electrocatalytic Voltammetry [16], electrochemiluminescence [17]. However, using this instrumental technique osmium was determined, but it involves many complicated steps and severe interferences of other metal ions. Furthermore the determination of osmium by the use of simple spectrophotometric methods has still the advantage of simplicity and doesn't require expensive or complicated test equipment.

* Corresponding author.
E-mail address: maanuse@gmail.com (M.A. Anuse).

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Research Article

Extractive Spectrophotometric Determination of Platinum in Cisplatin Injection, Alloys and Catalysts Assisted by 2-nitrobenzaldehydethiocarbohydrazone

Sunil B. Zanje[1], Arjun N. Kokare[1], Vishal J. Suryavanshi[1], Gurupad D. Kore[1], Balaji T. Khogare[1], and Mansing A. Anuse[1]*

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Abstract

A simple, rapid, selective and sensitive spectrophotometric method for the determination of platinum(IV) was developed, based on the color reaction between platinum(IV) and 2-nitrobenzaldehydethiocarbohydrazone (2-NBATCH) in the pH range 6.4-7.8. The red colored species have been developed after heating the reaction mixture in boiling water bath for 5 min and it was extracted into chloroform. The complex has an absorption maximum at 440 nm. A 20 fold of excess of reagent was required for complete complex formation. Beer's law was obeyed for platinum(IV) concentration in the range of 4-12 μg mL^{-1} and the optimum concentration range was 6-12 μg mL^{-1} of platinum(IV) as evaluated by Ringbom's plot. The molar absorptivity and Sandell's sensitivity were 1.03×10^4 L mol^{-1} cm^{-1} and 0.0189 μg cm^{-2}, respectively. The effect of pH, heating and extraction time, concentration of reagent and interference from various ions were investigated. The stoichiometry of the extracted complex was determined by Job's method of continuous variation, mole ratio method and slope ratio method. It was found that metal to ligand ratio was 1:2. The developed method has been successfully applied to the determination of platinum(IV) in pharmaceutical samples, catalyst and synthetic alloy sample.

Keywords: Platinum(IV); Spectrophotometry; 2-Nitrobenzaldehydethiocarbohydrazone; Analysis of real samples

1. Introduction

Platinum is a rare element, however, its use has increased in recent years and is grouped among the most precious metals (http:/unctad.org/infocomm/anglais/platinum/uses.htm). The consumption of platinum is in ornaments and jewellery and in different industries like automobiles in catalytic

*Corresponding e-mail: maanuse@gmail.com
1 Analytical Chemistry Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur-416004, India

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Original Article

Rapid removal of cadmium(II) from real samples by using N-*n* -octylcyclohexylamine: liquid-liquid extractive anion exchange study

Arjun N. Kokare[a], Sunil B. Zanje[a], Vishal J. Suryavanshi[a], Ganesh S. Kamble[a], Mansing A. Anuse[a]*

a*Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur, 416 004, Maharashtra, India.*

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Abstract

A simple and rapid liquid-liquid extractive system was developed for Cd(II) with N-*n* –octylcyclohexylamine (N-*n*-OCA) in a mixture of DCM and xylene. Extraction of Cd(II) was found to be quantitative in hydrochloric acid medium (6-8 M). Extracted ion-pair complex was back stripped with 3 M nitric acid (3 x 10 mL) and was determined by EDTA titrametrically. The stoichiometry of the extracted ion-pair complex was determined by slope analysis method and it was found as 1: 2: 1 (metal: acid: extractant). Various parameters like acid concentration, concentration of N-*n*-OCA, equilibrium time, effect of diluents were optimized for quantitative extraction of Cd(II). The applicability of the proposed method was studied for diverse ions, binary separation, multicomponent mixtures, alloy samples as well as separation Cd(II) from cigarette tobacco sample.

Key words: Liquid-liquid extraction; Cadmium(II); N-*n*-octylcyclohexylamine(N-*n*-OCA).

1. Introduction

Environmental pollution is a serious increasing problem that it controlled need necessary against action. A large amount of toxic micro-organic and organic materials has recently discharged into the nature resource from industries waste and cause serious air pollution, soil pollution and water pollution due to contaminated harmful chemical materials [1]. The toxic metals are also found in various manufacturing industries such as paint industries, coating industries, mining, metallurgical processes, nuclear power plants and many other industries. The toxic metal (element) separation from industrial waste is compulsory before discharging it in the environment. Among the toxic metals, cadmium ion has attention toward the health because of its harmful nature [2, 3].

Many attempts are being accomplished to investigate power and efficient techniques for separation or keep down the cadmium concentration in the wastewater or industries (sewer water) effluents to save the environment. Based on the concentration of cadmium effluents (waste water) and associated other ion (financial value) cost of treatment, so many processes carried out e.g., physical treatment (ion exchange) adsorption form (location) and separation process. (Reverse osmosis, ultra filtration and solvent extraction). A chemical precipitation technique also used today [4-8].

Solvent extraction processes or liquid-liquid extraction processes with organic liquid extractant in mixer-settler type reactor (SX). This technique most used for recovery and removal of the heavy metal in hydrometallurgy processes. It is fascinating technology for separating and enriching metal ion from lower concentration solution based on the exact choice of (highly) extremely selective extractant molecule for in demanded metal [9].

The various extracts was used for the extraction of Cd(II) such as amine [10-12], ketoximes [13], organic phosphorus extractants, carboxylic acid [14], different varieties of oganophosphorus-based extractants, viz. Di-2-ethyl hexyl phosphoric acid (D2EHPA) [15-18], bis(2,4,4-trimethylpentyl) phosphoric acid (Cyanex-272) (19-20), bis(2,4,4-trimethylpentyl) thiophosphinic acid (Cyanex-302) [21-23], trioctylphosphine oxide (Cyanex-921) [24], and Cyanex-923 (a mixture of various trialkylphosphine oxide) [25-26], Aliquat 336 [27], hexaaceto calyx(6)arene [28], phosphoric acid extractant (D2EHPA) and oxime extractant (MEX) in kerosene [29] have been utilize for the solvent extraction and separation of Cd(II) across other metal among of these extractant.

In the present method proposed an effective extractive approach for the removal of Cd (II) using a long-chain amine N-*n*-octylcyclohexylamine (N-*n*-OCA). We have reported from this laboratory, N-*n*-octylcyclohexylamine have been successfully employed for the solvent extraction and determination of tellurium(IV), selenium(IV) [30], germanium(IV) [31]. A major feature of

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Gold-Ions-Mediated Diproline Peptide Nanocarpets and Their Inhibition of Bacterial Growth

Ramesh Singh,[a] Vishal Suryavashi,[a] Vandana Vinayak,*[b] and Khashti B. Joshi*[a]

The structurally rigid dipeptide Pro-Pro, known to self assembled into well defined dumbbells followed by robust three dimensional copper embedded discs under the appropriate physicochemical conditions. Now the assembly of dipeptide Pro-Pro in the presence of Ag(I) and Au(III) metal ions was studied followed by its application as potential antibacterial agents. In the presence of Au(III) ions, ordered two dimensional sheets of submicron dimensions were obtained whereas in the presence of Ag(I) ions mostly random aggregates were found. Microscopy and spectroscopic study revealed that the Pro-Pro-Au(III) structures, in essence, can be considered as toxic metal ion "reservoirs" and can provide batter platform to target bacterial membrane. The antibacterial assay demonstrated that owing to high biocompatibility Pro-Pro dipeptide with bacterial cell, this simplest dipeptide worked as metal ion delivery agent and therefore it can show great potential in locally addressing bacterial infections.

The study of bio-organometallic chemistry confirmed that the activity of about one third of enzymes/protiens depends upon the nature of their respective metal ions.[1–3] Most of the metal ions are biologically relevant and involved in different biological activities.[3–4] Transition metals are important to the chemistry of living systems owing to their different and unique coordinating sites. The presence of the metal ions is responsible to the orientation of the substrate with different mode depending on the nature of binding site or group of proteins and hence play an important role in the biological processes.[5–8] Each protein has specific functionality even coordinates with same metal due to the presence of multifunctional α-amino acids backbone.

[a] *R. Singh, Dr. V. Suryavashi, Dr. K. B. Joshi*
Department of Chemistry,
School of Chemical Science and Technology,
Dr. Harisingh Gour Central University,
Sagar, MP, 470003, India,
E-mail: kbjoshi77@gmail.com

[b] *Dr. V. Vinayak*
Dr. Vandana Vinayak,
Diatom Nanoengineering and metabolism lab (DNM),
School of Applied Sciences,
Department of Criminology and Forensic Science,
Dr. Harisingh Gour Central University,
Sagar-M.P. 470003, India,
E-mail: kapilvinayak@gmail.com

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Certian metal containing cofactors are essential to carry out a particular biological function.[9–10] This interplay in the form of metalloproteins has extensively explored and is involved in several key biological processes, energy production and the synthesis of DNA building blocks. The study of the interaction of metal ions in an uncomplicated system such as model amino acid/peptide can reveal the relative energetic contribution of metal to protein folding and stability.[11] Therefore morphological changes in an appropriate test peptide/amino acid, in the presence of metal ions, can easily be studied via changes in secondary structural conformations. The outcome of this study motivates to transmit their physiological regulatory functions, such as, molecular and electron transportation in enzymatic redox reactions.[12–15]

The study of self assembly of short peptide conjugates simplified the structural complication and physiological activity of natural proteins. Therefore the formation of biocompatible nanomaterials by using peptide conjugates publicised for wide applications in biotechnology and medicinal chemistry.[16–20] L-proline, a rotationally constrained rigid ring structured amino acid, plays an important role in the destabilisation and stabilisation of several structural protiens.[21–23] Biologically relevant transition metal ions can be used to simplify the rigidity of proline based rich peptides via influencing their secondary structures and hence the self assembly. This strategy will be useful to find out the functioning of metal ions in the corresponding biological system.[5,24–26]

Previous reported results by our group demonstrated that the dumbbell shaped self assembly of structurally rigid Pro-Pro dipeptide was triggered into well defined robust disc[27] in the presence of copper ions solution. It is further proposed that these discs act as copper ions reservoirs and therefore the use of dumbbells and discs can control nutritional imbalance of copper in an affected site.[27] Our interest in short peptide based self assembly and its applications[28–31] further encouraged us to check the effect of other two metals of the group e.g. gold and silver which also admits there candidacy in biological systems. Gold is a non toxic element but it is a neurotoxin in the form of its salt (like $AuCl_3$) and cause nonessential neuropathy. Chrysotherapy applied for curing an inflammatory disease, rheumatoid arthritis found in the joints done by gold(I) ions.[32] Several gold metallodrugs are developed for various disease such as penicillamine, psoriatic arthritis, levamisole, and for various inflammatory skin disorders.[32,34] In recent research it is found that gold(I/III) complexes retained as a potential antitumor drugs and significantly exhibit cytotoxicity for cancer cells.[35] Similarly

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Highly proficient extraction separation of thorium(IV) from sulfuric acid solution using *N-n*-decylaniline: real sample analysis

Makrand M. Patil[1] · Vishal J. Suryavanshi[1,2,3] · Abhijeet G. Mulik[1] · Ganpatrao N. Mulik[1]

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Abstract
Herein we have developed solvent extraction method for thorium(IV) with 0.15 M *N-n* decylaniline in xylene from 0.5 M H_2SO_4. Physicochemical parameters like acid concentration, amine concentration, equilibrium time, phase ratio, diluent, loading capacity to name a few were optimized for the quantitative extraction of thorium(IV). The back-extraction of thorium(IV) from organic phase was done with 0.1 M nitric acid and determined complexometrically. To extend the utility of this method, binary and ternary mixture separation, extraction of thorium(IV) from monazite sand and gas mantle are also investigated.

Keywords Thorium(IV) · *N-n*-decylaniline · Extraction · H_2SO_4

Introduction

Nuclear technology is an attractive alternative to gain energy because of increasing energy requirements and the threat of global warming due to CO_2 release caused by coal and hydrocarbon burning [1]. Thorium is a radioactive element commonly used in nuclear plants. At today mostly satisfying the energy need of the world was depend on the thorium as the reserves of thorium on the earth is much more abundant than uranium, and thorium can be directly turned into uranium in a nuclear reactor [2]. Though thorium is observed in the many ores, its main source in India is monazite ore, thorianite, thorite and thoganite [3]. In process able ores, thorium found in association with uranium and zirconium, hence its extraction and separation is an essentiality. Liquid–liquid extraction is the most used separation technique for production processes and for analytical sampling. Hence, the precise and selective method of estimation of thorium is the need of time. The numbers of researcher groups are working on the estimation of radioactive elements from the environment. Recently, thorium(IV) with uranium(VI), zirconium(IV) was estimated from perchlorate media using PC-88A [4]. Thorium(IV) was extracted by using bis-2-(butoxyethylether) [5]. The extractive behavior of uranium(VI) and thorium(IV) was done by using TBPO [6] in salicylate medium. Cyanex 301 and Cyanex 302 [7], Cyanex 923 [8] were successfully used for the extractive separation of thorium(IV). Apart from that the extraction study of thorium(IV) was also investigated by several extractants like di-(2-ethylhexyl) 2-ethylhexyl phosphonate [9] bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) [10]. Amberlite LA-1 or LA-2 [11], *N*-methyl-*N*,*N*,*N*-trioctylammonium chloride [12] mixture of *N-n*-octylaniline and trioctylamine [13] are successfully employed for the extraction of thorium(IV). Extraction of thorium(IV) was done from 2-octylaminopridine [14] in kerosene along with various organophosphorus compounds like TBP (30%) [15], Cyanex302 [16], triphenylphosphine oxide, di-isodecyl phosphoric acid [17–20] as well as Di 1(methyl-heptyl) methyl phosphonate [21], The extraction of Th(IV) was investigated by using di(1-methyl-heptyl) methyl phosphonate (DMHMP) in kerosene as an extractant [22].

The chain length of various high molecular weight amines playes an important role in the extraction process. The extraction of thorium(IV) was investigated via number of long chain high molecular weight amines such as *N*-heptylaniline [23], *N-n*-octylaniline [24] which shows that, as chain length increases extraction is also increases with decreasing concentration of amine (Table 1). Hence,

✉ Ganpatrao N. Mulik
ganpatraomulik@rediffmail.com

[1] Department of Chemistry, Balwant College, Vita, Maharashtra 415311, India

[2] Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur, Maharashtra 416004, India

[3] Department of Chemistry, PVPIT Budhgaon, Sangli, Maharashtra 416304, India

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Liquid–liquid extraction of uranium(VI) from weak sodium acetate medium using 2-octylaminopyridine: real sample analysis

Gurupad D. Kore[1,2] · Sunil B. Zanje[3] · Arjun N. Kokare[1] · Vishal J. Suryavanshi[1] · Mansing A. Anuse[1] · Sanjay S. Kolekar[1]

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Abstract
The analytical technique has been developed for the extraction and determination of uranium(VI). This process is based on the ion-pair complex formation of uranium(VI) with 2-octylaminopyridine in xylene. Uranium(VI) is quantitatively extracted by optimizing the parameters of solvent extraction in presence of sodium acetate, such as pH, concentration of weak organic acids, strippant, shaking period, solvent study, and concentration of extractant. A mechanism of extraction was proposed based on the slope ratio analysis method. The interference of various cations and anions was also investigated. The versatility of the developed method was investigated by employing it to binary and ternary mixtures. The robustness of the method was demonstrated by determining uranium(VI) in the bone sample.

Keywords Solvent extraction · Uranium(VI) · 2-octylaminopyridine · Sodium acetate · Bone sample

Introduction

Uranium is the most vital element for nuclear energy [1]. It is universal that uranium is toxic and is being radioactive; thus the safety profiles for uranium compounds are well established [2]. Hence it is one of the elements for which world health organization (WHO) norms are most stringent (30 µg/L) in drinking water. This is because uranium is a relatively contaminating element in many surface or near-surface environments, its geological exploration requires the measurement of trace quantities of metal ions in water and other samples [3–5]. The natural source for uranium is monazite which contains a sizeable amount of uranium. Consequently, the separation purification of uranium is of great practical importance. The methodology adopted for extraction and purification from ore and nuclear fuel reprocessing has always attracted the attention of separation scientists. The efficient and selective extraction of uranium from aqueous solution has been a subject of significant interest because of the global shortage of uranium sources and radioactive contaminants in the environment, soil, water in which versatile new materials that can separate efficiently desired ore [6–8].

A large number of modern analytical tools have been available for the determination of uranium in a wide variety of samples, The increasing availability of powerful instrumental techniques such as neutron activation analysis (NAA), energy dispersive X-ray fluorescence (EDXRF), inductively coupled plasma atomic emission spectrometry (ICP-AES); inductively coupled plasma emission mass spectrometry (ICP-MS) has enabled the analysis of complex mixtures with high accuracy and precision [9–14]. Even though these techniques provide high sensitivity and favorable detection limit, their application requires rather expensive equipment and leads to higher running cost [15]. Generally, solvent extraction and spectrophotometric technique are widely used to separate and determine uranium(VI) [16–20].

In this context, attentions have been given for the development of soft donor complexing agents as extractants for Ln/An separation. Relatively soft donor atom such as nitrogen prefers 5f elements than 4f elements, providing the higher selectivity than harder oxygen atoms. Concerning high molecular weight, amines act as better extractant

✉ Gurupad D. Kore
gdkore1027@gmail.com

[1] Analytical Chemistry Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur 416004, India

[2] Department of Chemistry, Padmabhushan Vasantraodada Patil Mahavidyalaya, Kavathemahankal, MS 416405, India

[3] Department of Chemistry, J. M. Patel Arts, Commerce and Science College, Bhandara, MS 441904, India

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CHAPTER

16

Photosynthetic microalgal microbial fuel cells and its future upscaling aspects

Mohd Jahir Khan[1], *Vishal Janardan Suryavanshi*[2], *Khashti Ballabh Joshi*[2], *Praveena Gangadharan*[3] *and Vandana Vinayak*[1]

[1]Diatom Nanoengineering and Metabolism Laboratory (DNM), School of Applied Sciences, Dr. Harisingh Gour Central University Sagar, Sagar, India [2]School of Chemical Science and Technology, Department of Chemistry, Dr. Harisingh Gour Central University Sagar, Sagar, India [3]Department of Civil Engineering, Indian Institute of Technology, Palakkad, India

16.1 Introduction

With an increase in globalization and industrialization, recent studies show that electricity production by solar panels, wind power, and hydropower stations faces challenges to fulfill the current demand for electricity by electric vehicles (EVs) [1]. However, lithium ion (Li^+) batteries, which are an alternative solution to conventional power storage for EVs are not feasible in many countries where neither Li^+ reserves nor Li^+ manufacturing industries exist [2–4]. Hence there is need for a stable and renewable energy source for the production of electricity [5]. Even though EVs run by electricity and are superior to gasoline in having zero carbon emissions [6], a discontinuity in electricity supply may switch them back to gasoline vehicles, hence not only a continuous and reasonable electricity supply but also gasoline and biofuel with a zero-carbon footprint is the need of an hour [7]. A lot of research has been done on alternative sources to generate electricity and gasoline reservoirs to run hybrid electric vehicles which operate by both electricity and gasoline. Such renewable resources should have the following attributes: readily available, abundant, feasible, economical, and have zero carbon emissions [8,9]. A report from the International Energy Agency shows that biofuels from renewable energy resources

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META

Liquid-liquid extraction of uranium (VI) using Cyanex 272 in kerosene from sodium salicylate medium

Kamble, Pravin N. (Analytical and Environmental Research Lab, Department of Chemistry, Shivaji University, Kolhapur (India)); Mohite, Baburao S. (Analytical and Environmental Research Lab, Department of Chemistry, Shivaji University, Kolhapur (India)); Suryavanshi, Vishal J. (Balwant College, Vita Talkhanapur, Sangali (India)); Salunkhe, Suresh T. (Balwant College, Vita Talkhanapur, Sangali (India)), E-mail: pravin_in85@rediffmail.com

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Abstract

[en] Liquid-liquid extraction of uranium (VI) from sodium salicylate media using Cyanex 272 in kerosene has been carried out. Uranium (VI) was quantitatively extracted from $1x10^{-4}$ M sodium salicylate with $5x10^{-4}$ M Cyanex 272 in kerosene. It was stripped quantitatively from the organic phase with 4M HCl and determined spectrophotometrically with arsenazo(III) at 600 nm. The effects of concentrations of sodium salicylate, metal ions and strippants have been studied. Separation of uranium (VI) from other elements was achieved from binary as well as from multicomponent mixtures. The method is simple, rapid and selective with good reproducibility (approximately ±2%). (author)

Primary Subject

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Ion-pair based liquid–liquid extraction of gold(III) from malonate media using 2-octylaminopyridine as an extractant: analysis of alloys, minerals, and drug samples

Vishal SURYAVANSHI[1,2], Arjun KOKARE[2], Sunil ZANJE[2], Abhijeet MULIK[1], Rupali PAWAR[1], Makrand PATIL[1], Ashwini GAIKWAD[2], Mansing ANUSE[2], Ganpatrao MULIK[1,*]

[1]P. G. Department of Chemistry, Balwant College, Vita, Sangli, Maharashtra, India
[2]Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University Kolhapur, Maharashtra, India

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Abstract: Liquid–liquid extraction of Au(III) from aqueous sodium malonate medium using 2-octylaminopyridine (2-OAP) as an extractant in xylene was achieved. The current work explored the influence of several experimental parameters such as pH, weak acid concentration, extractant concentration, equilibrium time, stripping agents, and aqueous:organic volume ratio on the extraction of Au(III). The experimental results showed that the Au(III) was quantitatively extracted to about 99.5% by 0.05 M 2-OAP in 0.05 M malonate at 5.0 pH. Ammonia solution was used to strip the gold-loaded organic phase and about 99.5% of Au(III) was reversibly extracted into the aqueous phase. Gold(III) was extracted into the organic phase via formation of ion-pair complex [2-OAPH$^+$.Au $(C_3H_2O_4)_2^-$]. The stoichiometry of the extracted species was 1:2:1 (metal: acid: extractant) determined by slope analysis. The method affords the binary, ternary mixture separation as well as separation of Au(III) from synthetic mixtures and alloys. The method is applicable for the determination and separation of gold from ayurvedic samples and recovery of gold from e-wastes. A reproduction of the method was checked by finding relative standard deviation for n = 5, which was 0.29%, and the limit of detection was 1.08 μg/mL.

Key words: Liquid-liquid extraction, gold(III), sodium malonate, 2-octylaminopyridine (2-OAP), e-wastes, ayurvedic samples

1. Introduction

Gold is a rare precious metal with high economic value. The gorgeousness and high luster of gold have led its use in jewelry and currency and as a standard for monetary systems throughout the world. Gold displays noteworthy applications in medicine, dentistry, industry, electronics, catalysts, cosmetics, and even in food and drinks.[1–3] Some gold salts have antiinflammatory properties depicted by their use in the treatment of arthritis and other similar conditions.[4–6] However, only salts and radioisotopes of gold are of pharmacological value, as elemental (metallic) gold is inert to all the chemicals it encounters inside the body. Due to the increasing demand for gold in the industrial sector and its scarcity, there is an immense need for its recycling. In general, gold is separated and purified from industrial wastes by hydrometallurgical processes involving chloride media.[7] Solvent extraction techniques have been widely employed for the recovery of precious metals from chloride

*Correspondence: ganpatraomulik@rediffmail.com

Analytical Methods

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2-Octylaminopyridine assisted solvent extraction system for selective separation of palladium(II) ion-pair complex from synthetic mixtures and real samples

Vishal J. Suryavanshi,[ab] Rupali R. Pawar,[b] Mansing A. Anuse*[a] and Ganpatrao N. Mulik*[b]

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Herein, 2-octylaminopyridine (2-OAP) amine is used in the liquid–liquid extraction of palladium(II) from aqueous salicylate media. It is found that pH does not affect the metal extraction process in the pH range of 1.8–2.4. Palladium(II) complex formation was verified by a log–log plot, whereas from the slope analysis, the ion pair complex stoichiometry 1 : 1 (metal : ligand) and 1 : 3 (metal : acid) was confirmed. The extraction system was optimized for the choice of diluent (xylene) as well as for the effective stripping agent (5.0 M ammonia). The selectivity for palladium(II) was found to be maintained when the organic phase (0.03 M 2-OAP in xylene) is used to extract the palladium(II). The extraction saturation capacity of palladium(II) was determined from 0.02 M sodium salicylate solution with 10 mL 0.03 M 2-OAP, and its experimental value exceeds 2.5 mg under the experimental conditions. Stripping of palladium(II) from the loaded organic phase was performed with 5.0 M ammonia. The extraction with varying parameters like equilibrium time, temperature, diluents, concentration of extractant, loading capacity, regeneration power and stability of extraction was also studied. The extraction behavior of associated metals, namely, noble metals and base metals, has been investigated, and the conditions for binary separation involving these metal ions have been optimized. Based on the extraction protocol, palladium(II) has been recovered from real samples.

1. Introduction

Increasing demand for noble metals, particularly platinum group metals (PGMs), such as palladium(II), platinum(IV), ruthenium(III), rhodium(III), *etc.* has been observed because of their wide range of industrial applications, *e.g.* as catalysts in organic processes, value added components in metal alloys and vehicle catalytic converter systems, in jewelry, and in chemical, pharmaceutical, petroleum and electronic industries. These applications of PGMs have increased the demand for these metals, whereas the natural resources are limited.[1,2] Therefore, the gap between the demand and supply from natural sources must be replenished by recycling of spent materials, especially spent vehicle catalysts containing these metals. Processes of separation and purification of PGMs are difficult and complicated due to their chemical properties and the formation of many chemical species in chloride media.

Solvent extraction also known as liquid–liquid extraction is a process that allows separation of two or more components, *e.g.* metal ions making use of their unequal solubilities in two immiscible liquid phases. Different types of solvents have been employed for extraction of specific species. Very recently, a new class of solvents, namely switchable solvents, has also been developed for the extraction as they facilitate economically competitive and environmentally conscious views and can be removed from products without distillation.[3–7] Specifically, solvent extraction is a suitable method for removal of PGMs from low concentrated sources, because it offers a number of advantages like high selectivity and metal purity. In addition, more efficient removal of metals is possible by the use of multi-stage extraction. Traditionally, the hydrometallurgical recovery of PGMs by solvent extraction processes is based on the fact that noble metal ions can easily form species that are extractable into the organic phase with various reagents.[8,9] Many different extractants have been studied and proposed, including dialkylsulphides and sulphoxides,[10–13] phosphonium extractant,[14] quaternary phosphonium salt,[15] alamine 300,[16] hydroxyoximes and ketoximes,[17–20] hydrophobic amines and quaternary ammonium salts,[21–26] organophosphorus extractants,[27–31] pyridinecarboxamides,[32,33] and *N*-*n*-octylaniline.[34–38]

In our earlier work, we have reported the liquid–liquid extraction of palladium(II) with high molecular weight amine (HMWA) such as *N*-*n*-octylaniline from hydrochloric acid[34] and

[a]*Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur-416004, Maharashtra, India. E-mail: maanuse@gmail.com*

[b]*Department of Chemistry, Balwant College, Vita-415311, Maharashtra, India. E-mail: ganpatraomulik@rediffmail.com*

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Extraction of iridium(III) by ion-pair formation with 2-octylaminopyridine in weak organic acid media

Vishal J. Suryavanshi[a,b], Makrand M. Patil[b], Sunil B. Zanje[a], Arjun N. Kokare[a], Gurupad D. Kore[a], Mansing A. Anuse[a], and Ganpatrao N. Mulik[b]

[a]Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University Kolhapur, Maharashtra, India; [b]P. G. Department of Chemistry, Balwant College, Maharashtra, India

ABSTRACT

To extract iridium(III), various physicochemical parameters were studied. 2-Octylaminopyridine was used for the extraction of iridium(III) from acetate medium at 8.5 pH. Quantitative extraction of iridium (III) was achieved via ion-pair formation of cation [2-OAPH$^+$] and anion [Ir(CH$_3$COO)$_4$]$^-$. The stripping of iridium(III)-laden organic phase was carried out 2 M HCl (3 × 10 mL) . The stoichiometry of the extracted ion–pair complex was found to be 1:4:1 (metal: acetate: extractant). The extracted species [2-OAPH$^+$. Ir(CH$_3$COO)$_4^-$] is assumed to be an ion association product of [Ir(CH$_3$COO)$_4$] $^-$ and [2-OAPH]$^+$. The proposed method was successfully used in the separation of iridium(III) from binary and ternary mixtures. Analysis of various alloy samples was also carried out.

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Alloy analysis; iridium(III); sodium acetate; solvent extraction; 2-Octylamiopyridine

Introduction

Iridium is a very rare and precious platinum group metal (PGM) whose abundance is extremely low, typically about 2 ppb. It is mostly found together with osmium in the alloys, osmiridium/syserkite and iridosmine/neuyanskite. Because it has a wide range of applications and its growing economic impact, iridium has been widely used in the making of alloys, dental alloys, jewellery, electrical equipment for industrial applications (*e.g.* electronics and catalyst industry), exhaust gas catalyst, corrosion-resistance, chemical wares, crucibles for high-temperature reactions and extrusion dyes for high-melting glasses.[1,2] It is used in the making of alloys with platinum to yield highly resistant anodes,[3] high-temperature crucible,[4] catalyst for the electrocatalytic reduction of carbon dioxide-[5] and specific catalysts in organic chemistry.[6] It is also used as electrodes together with platinum in spark plugs in internal combustion engines. Such spark plug electrodes usually range between 5 and 15% in mass of iridium, the rest being composed of platinum.[7] Besides, it is also used in the field of photography and aviation. Since the natural resources of iridium metal are limited, we could not fulfil its demand[8] and the demand for iridium will continue to grow[9] in the future.

It is important to find an effective separation process to recover iridium metal with high purity from diverse secondary resources. The process of separation and purification of iridium is difficult and complicated due to its similar chemical properties as other PGMs and the formation of many chemical species. Solvent extraction is a process that allows the separation of two or more components, based on the solubilities in two immiscible liquid phases. Liquid–liquid extraction is a very good method for the removal of PGMs from leaner sources, as it has a number of advantages like high selectivity and metal purity. Solvent extraction is based on the fact that the PGMs can form species easily, which is extractable into the organic phase with various reagents.[10]

Several extraction methods have been developed for the extraction of iridium(III). The extraction of iridium (III) from its chloride solution was carried out using commercially available solvent extraction reagents like trioctylphosphine oxide,[11] cyanex 923,[12–14] cyanex 921,[14] cyanex 471,[14] cyanex 272,[14] LIX 54,[14] LIX 860N-I,[14] TBP,[14] cyanex 471X,[15] alamine 336 and TBP.[16] The extraction behaviour of metal impurities normally associated with iridium(III) was examined and the extraction method is applied for sample analysis. The high molecular weight amines

CONTACT Mansing A. Anuse maanuse@gmail.com Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University Kolhapur-416004, Maharashtra, India; Ganpatrao N. Mulik ganpatraomulik@rediffmail.com P.G. Department of Chemistry, Balwant College, Vita-415311, Maharashtra, India.

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Journal of Colloid and Interface Science
Volume 609, March 2022, Pages 734-745

Amorphous nickel tungstate films prepared by SILAR method for electrocatalytic oxygen evolution reaction

D.B. Malavekar [a], V.C. Lokhande [b], D.J. Patil [c], S.B. Kale [a], U.M. Patil [a], T. Ji [b], C.D. Lokhande [a]

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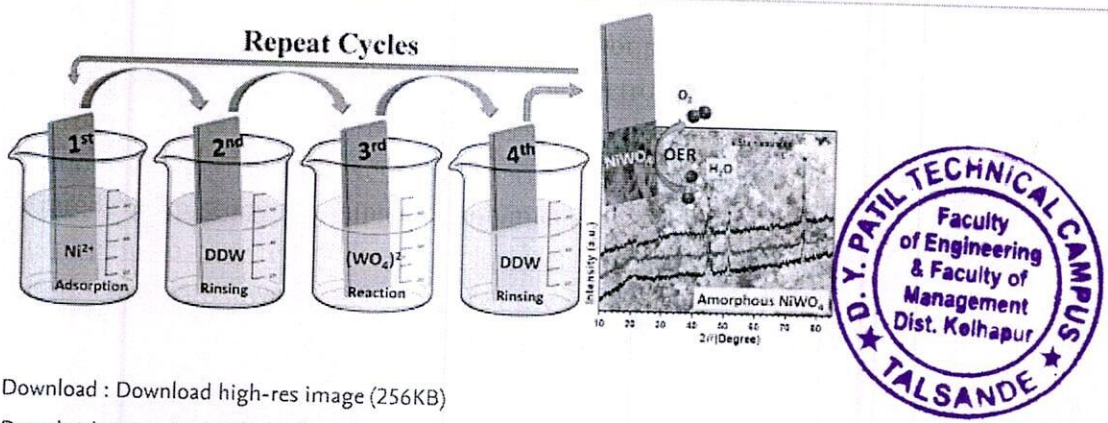
Abstract

Development of electrocatalyst using facile way from non-noble metal compounds with high efficiency for effective water electrolysis is highly demanding for production of hydrogen energy. Nickel based electrocatalysts were currently developed for electrochemical water oxidation in alkaline pH. Herein, amorphous nickel tungstate ($NiWO_4$) was synthesized using the facile successive ionic layer adsorption and reaction method. The films were characterized by X-ray diffraction, Raman spectroscopy, Fourier transfer infrared spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy techniques. The electrochemical analysis showed 315 mV of overpotential at 100 $mAcm^{-2}$ with lowest Tafel slope of 32 mV dec^{-1} for oxygen evolution reaction (OER) making films of $NiWO_4$ compatible towards electrocatalysis of water in alkaline media. The chronopotentiometry measurements at 100 $mAcm^{-2}$ over 24 h showed 97% retention of OER activity. The electrochemical active surface area (ECSA) of NW120 film was 25.5 cm^{-2}.

Graphical abstract



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Keywords

Amorphous electrocatalyst; Nickel tungstate; Successive ionic layer adsorption and reaction (SILAR); Thin film, Water electrocatalysis

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Energy Technology / Volume 10, Issue 8 / 2200295

Research Article

Binder-Free Synthesis of Mesoporous Nickel Tungstate for Aqueous Asymmetric Supercapacitor Applications: Effect of Film Thickness

Dilip J. Patil, Dhanaji B. Malavekar, Vaibhav C. Lokhande, Prity P. Bagwade, Sambhaji D. Khot, Taeksoo Ji, Chandrakant D. Lokhande ✉

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Abstract

Nickel tungstate thin films of different thicknesses are synthesized using the binder-free successive ionic layer adsorption and reaction (SILAR) method at ambient temperature and subsequent calcination at a temperature of 727 K. The physicochemical characterizations of $NiWO_4$ thin films are carried out using different techniques. The electrochemical performances of $NiWO_4$ films are evaluated in 2 M KOH electrolyte using a standard three electrode system. The specific capacitance of 1536 F g^{-1} at the current density of 2 A g^{-1} is obtained for the $NiWO_4$ film. The film exhibits excellent electrochemical stability of 87% after 5000 galvanostatic charge–discharge (GCD) cycles at the current density of 3 A g^{-1}. This study highlights use of SILAR-deposited $NiWO_4$ thin films as a cathode in aqueous asymmetric supercapacitors (ASCs). The ASC device $NiWO_4$/KOH/Fe_2O_3 exhibits a specific capacitance of 115 F g^{-1} at 2 A g^{-1} and specific energy of 23Wh kg^{-1} at specific power of 1.2 kW kg^{-1}. The device shows remarkable electrochemical cycling stability (78% capacitance retention after 5000 GCD cycles). The SILAR-deposited $NiWO_4$ thin films are expected to emerge as a potential candidate for supercapacitors.

Conflict of Interest

The authors declare no conflict of interest.

Open Research

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

ScienceDirect

Synthetic Metals
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SILAR synthesized dysprosium selenide (Dy_2Se_3) thin films for hybrid electrochemical capacitors

S.D. Khot [a], D.B. Malavekar [a], R.P. Nikam [a], S.B. Ubale [a], P.P. Bagwade [a], D.J. Patil [a], V.C. Lokhande [b], C.D. Lokhande [a]

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Highlights

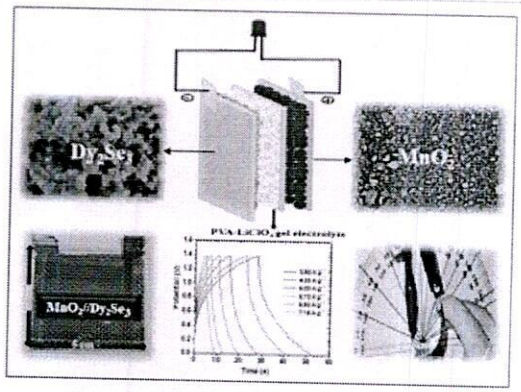
- The novel Dy_2Se_3 thin films were synthesized using successive ionic layer adsorption and reaction method.
- Dy_2Se_3 electrode exhibits specific capacitance of $92\,Fg^{-1}$ at current density of $2.85\,Ag^{-1}$.
- Hybrid device delivers $18\,Whkg^{-1}$ specific energy at $2.668\,kWkg^{-1}$.
- This hybrid device retained 92.82% of capacitance at a device bending angle of 160°.

Abstract

As the necessity of energy storage is continuously increasing, new materials have been investigated for electrochemical energy storage, especially for electrochemical capacitors. These storage devices are rapidly convertible as well as air pollution free. Therefore, a number of materials have been explored as electrode materials for supercapacitors to fulfill different requirements of electrochemical energy storage. Herewith, dysprosium selenide (Dy_2Se_3) films were prepared using the simple successive ionic layer adsorption and reaction (SILAR) method and characterized using different physico-chemical techniques. The specific capacitance (C_s) of $92\,Fg^{-1}$ was obtained at the current density of $2.85\,Ag^{-1}$ in 1M $LiClO_4$ electrolyte with a retention of 85% over 5000 galvanostatic charge-discharge (GCD) cycles performed at a current density of $4\,Ag^{-1}$. The flexible solid-state hybrid electrochemical capacitor of configuration $Dy_2Se_3/LiClO_4$-PVA/MnO_2 showed C_s of $83\,Fg^{-1}$ and specific energy of $18\,Whkg^{-1}$ at a specific power of $2.7\,kWkg^{-1}$. This hybrid device

retained 92% of capacitance at a device bending angle of 160°. These results demonstrate the facile synthesis of Dy_2Se_3 and its possible use in electrochemical energy storage applications.

Graphical Abstract



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International Journal of Hydrogen Energy
Volume 48, Issue 23, 15 March 2023, Pages 8465-8477

Nanocrystalline cobalt tungstate thin films prepared by SILAR method for electrocatalytic oxygen evolution reaction

P.P. Bagwade, D.B. Malavekar, V.V. Magdum, S.D. Khot, R.P. Nikam, D.J. Patil, U.M. Patil, C.D. Lokhande

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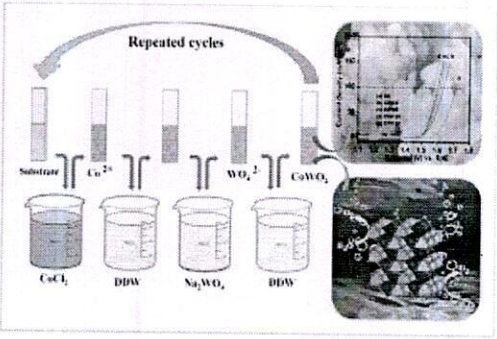
Highlights

- $CoWO_4$ thin film electrocatalysts prepared by SILAR method was employed for oxygen evolution reaction.
- The $CoWO_4$ material exhibited porous morphology with specific surface area of $49.3\,m^2g^{-1}$.
- $CoWO_4$ electrode exhibited excellent OER functioning with overpotential of 330 mV at a current density of $100\,mAcm^{-2}$.
- $CoWO_4$ thin film electrode exhibited remarkable stability (97%) after 24 h in 1 M KOH.

Abstract

This study highlights on the application of nanocrystalline cobalt tungstate ($CoWO_4$) thin films as an electrocatalyst for oxygen evolution reaction (OER) prepared using successive ionic layer adsorption and reaction (SILAR) method. The X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy etc. were employed for the characterization of $CoWO_4$ thin films, revealing the formation of crystalline $CoWO_4$ with spherical morphology. Furthermore, $CoWO_4$ showed excellent electrochemical performance with the overpotential of 330 mV and Tafel slope of $153\,mVdec^{-1}$ with retaining 97% of electrochemical stability after 24 h of OER. The study confirmed the structural maintenance of $CoWO_4$ thin films after stability study.

Graphical abstract



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Keywords

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Analysis of Model based Shadow Detection and Removal in Color Images

Ms. Trupti Ghewari
Student, Department of Electronics and Telecommunication Engineering
D. Y. Patil College of Engineering and Technology, Kasaba Bawada, Kolhapur
trupti.ghewari2018@gmail.com

Asso. Prof. S. R. Khot
Department of Electronics and Telecommunication Engineering
D. Y. Patil College of Engineering and Technology, Kasaba Bawada, Kolhapur
srkhot08@gmail.com

Mr. M. D. Khatavkar
Asst. Professor,
D. Y. Patil Technical Campus, Talsande, Kolhapur
mandar.khatavkar@gmail.com

Abstract—**Shadow detection and removal efficiency in color images has become most important requirement while processing aerial images. The successive thresholding scheme (STS) is presented in this paper. Scheme increases shadow detection accuracy. In this paper, we have modified ratio map to obtain accurate gap between shadow and non-shadow pixels. The idea is derived from original Tsai's method. The global thresholding scheme is used to classify the pixels into shadow and non-shadow class. The coarse map obtained for candidate shadow pixels is then processed using connected component and candidate shadow region pixels are grouped. The iterative method is used for detecting true shadow pixels. Experimental results show that, the shadow detection correctness of our suggested model based algorithm is analogous to Tsai's algorithm. Dataset of images is tested using both approaches to calculate precision (P), recall (R) and Fscore (F). The results show outstanding performance for our method.**

Keywords—Shadow detection, shadow removal, AHE, Otsu method, Shadow model.

I. INTRODUCTION

It has become much significant to detect and remove shadows from images and videos these days. Light orientation and object shape related deep information can be understood from regions where object shadows are present and masked due to shadows. It can be seen that, still there is of scope for improved shadow detection algorithms which are applicable for image handling and pattern recognition systems. The presence of shadows in images includes problems like, less accuracy of classification of background and foreground objects during image processing, lack of objects differentiation capability due to merging effects, object occlusions, change in actual colors and shapes. Also visual quality of objects is also affected due shadows present in image. Detection of shadow regions and removing them to get almost original information in that region is very much important preprocessing step in machine vision and image processing where feature extraction and related approaches are applicable.

To identify shadows of color aerial images, low luminance and deeply saturated blue or violet wavelength are two most important properties of shadows to be considered. The input aerial image in RGB color space is first converted into HIS color space to get the hue, saturation, and intensity values. Shadow region is then recognized and segmented by using saturation and intensity values. The shadow and non-shadow regions can be differentiated based on typical observations. For shadow regions mostly large hue value is seen. Also blue color value is quite low. Along with this if difference is taken between green and blue values then it is also very low. Using this observation three thresholds are defined based on which shadows can be identified. Based on available literature in recent relative works, the algorithm presented by Tsai has better efficiency in detection of shadows in color aerial images. In this algorithm, HSV and YCbCr color models are used. The luminance, chrominance and hue values are specifically calculated for the input image. Then ratio of hue to intensity is calculated to build the coarse shadow ratio map. The accuracy level is considerable using this algorithm.

II. RELATED WORK

The shadow detection and removal algorithm suggested by Tsai [1] is considered as comparative method. The processing of this method is as seen in introduction section. The dataset used is also considered for comparative analysis.

V. G. Mamde et al [2], have focused shadow affected area. This area is taken for segmentation, and by considering statistical features suspicious regions of shadows are extracted. Properties of objects and their spatial relationship are considered which are from these shadow regions, which are dark objects, are taken off. Color image transformation along with global thresholding and morphological erosion based convolution filtering is applied. There is an improvement in accuracy by observing the experimental analysis. Avalanche histogram equalization method is used for shadow removal.

Shugen Wang et al [3], have proposed image enhancement method. In this shadow detection and reparation is also considered as one of the process. For enhancing high resolution satellite images, the principal components analysis (PCA) is used to process the features. To remove shadows from the images, luminance in varied. Luminance based multi-scale Retinex (LMSR) algorithm is used for dynamic applicability of presenting the images with better and clear visual information. When luminosity of image is modified, the appearance may lead to loss of information which is preserved with the help of PCA which provides stability in orthogonal channels.

$$Iz(m, n) = Rz(m, n) \cdot Lz(m, n) \quad (3)$$

Where z ∈ R, G, B and '•' denotes multiplication in pixel-wise fashion. Due to shadows in the regions, reduction in illumination and image intensities which can be given by multiplicative scalars of Cz (m, n) .Thus, (3) can be extended to:

$$Iz(m, n) = Rz(m, n) \cdot Lz(m, n) \cdot Cz(m, n) \quad (4)$$

If log of equation (4) is taken then it can be seen that, shadow indicates an additive change in intensities. The additive shadow component reduction is done by variety of methods in the literature. The intelligent shadow detection method is required to separate shadows from black regions. Shadow detection can become more complicated due to presence of self-shading, inter-reflection, non-uniform shadow, shape of the item and the artefacts involved in image catching.

The shadow can be modeled and represented by following formula:

$$Ii = (ti \cos\theta i\ Lx + Ly)\ Ri$$

Where - Ii represents the value for the i-th pixel in RGB space. Lx and Ly represent the intensity of the direct light and environment light, similarly dignified in RGB space. Ri is the surface reflectance of that pixel. The angle between the direct lighting direction and the surface normal is denoted by θi. The attenuation factor of the direct light is given by ti.

In sunshine regions value of ti= 1 means, and in shadow regions value of ti = 0.

We denote by Ki = ti cosθi the shadow factor for the i^{th} pixel and by the ratio r =Lx/Ly. Lx represents direct light and Ly represents environmental light. To obtain shadow free region this coefficient is used to relight each pixel belonging to shadow region.

Algorithm Steps:

1. *Take input image*
2. *Prepare shadow ratio map*
3. *Morphological operations to get coarse shadow map*
4. *Process iteratively each pixel from map*
5. *Apply local thresholding to identify shadow or non-shadow pixel.*
6. *Form true shadow pixel set.*

C. Shadow Removal

Automatic detection of shadow regions and then remove even from simple images is our target work. While detecting all shadows is expected to remain hard, we make some constraints related to the images. The method used to detect and remove shadow is detailed in algorithm.

Algorithm Steps:

1. Accept the shadow detected image.

2. Convert the picture in the YCbCr color space. Compute Y-channel histogram.

3. Use Y channel values to compute full average of entire image.

4. Perform sliding window iteration through the image. The sliding window size is decreased iteratively

5. In order to find true shadow pixels from set obtained in step 4, we use two approaches:

a. Pixels which have equal value of average window intensity can be considered being part of the shadow.

b. Use sliding window technique to computer

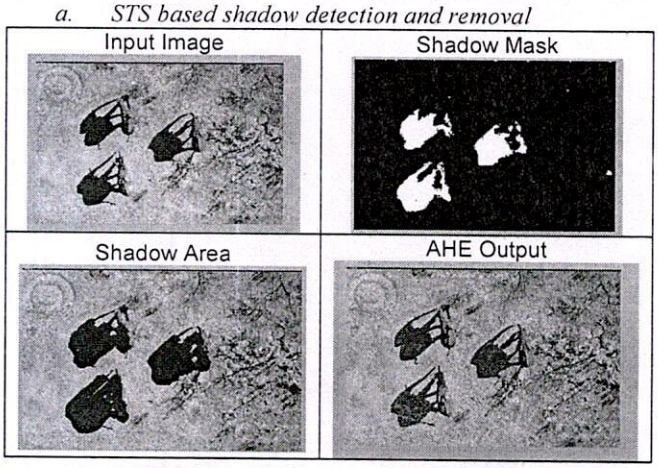
c. Compute the non-shadow point's average. the pixel is considered as part of shadow if it has intensity value of 70% window average intensity value.

6. Display the list quality parameter and display final resultant image.

IV. Results and Analysis

The algorithms for successive thresholding and model based shadow detection and removal is implemented in MATLAB. Image processing toolbox is used to handle images and process them. The results obtained are as shown in fig 1 and 2.

a. STS based shadow detection and removal



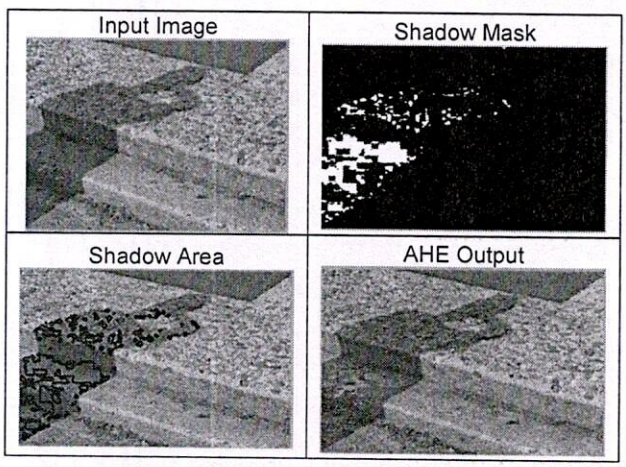


Image 8	0.83	0.41	0.761
Image 9	0.66	0.59	0.78
Image 10	0.62	0.51	0.52

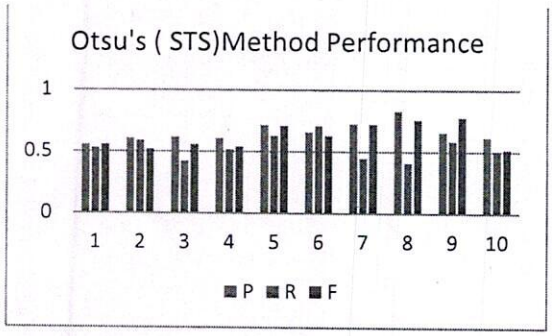


Fig. 3. Performance evaluation for Otsu's(STS) method

TABLE II. PERFORMANCE EVALUATION OF EACH IMAGE FOR P,R, F CALCULATIONS FOR MODEL BASED METHOD

Image Name	P Precision	R Recall	F Fscore
Image 1	0.81	0.63	0.56
Image 2	0.83	0.62	0.52
Image 3	0.86	0.63	0.51
Image 4	0.88	0.62	0.53
Image 5	0.78	0.78	0.52
Image 6	0.71	0.79	0.42
Image 7	0.79	0.62	0.63
Image 8	0.81	0.631	0.81
Image 9	0.82	0.63	0.71
Image 10	0.83	0.61	0.42

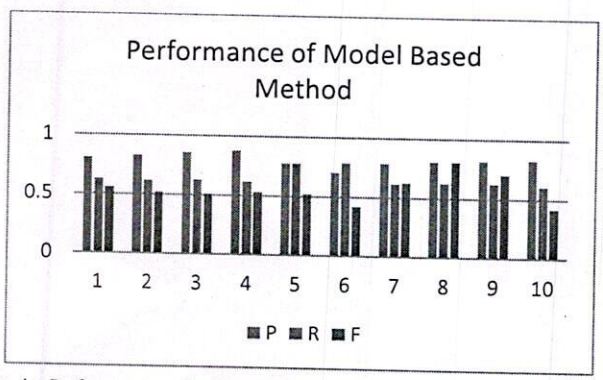


Fig. 4. Performance evaluation for model based method

TABLE III. COMPARATIVE ANALYSIS OF AVERAGE PERFORMANCE OF SHADOW DETECTION AND REMOVAL

Parameter	Otsu's (STS) method (average)	Model based method (average)
P	0.662	0.813
R	0.543	0.652
F	0.634	0.562

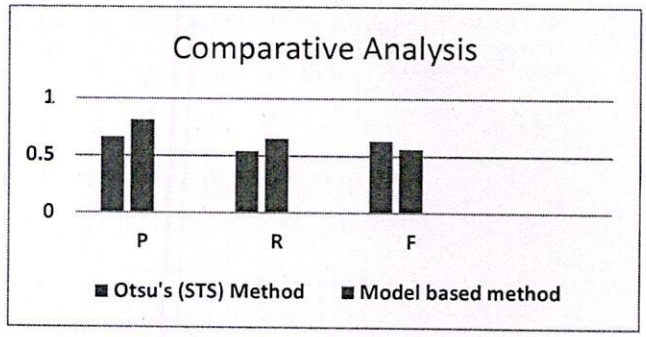


Fig. 5. Comparative analysis of Otsu's and model based methods.

V. CONCLUSION

The test results of the shadow detection and removal in aerial and outdoor color images is outperforming. The proposed method shows most accurate shadow region detection.The algorithm for aerial images was assessed in an experiment with number of images and the results were compared to other two techniques. The performance is good in terms of true shadow pixel detection, removal of shadow from image, accuracy levels of the entire process and computation time requirements.

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