



ISAS newsletter

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ISAS newsletter is a quarterly email publication of Indian Society of Analytical Scientists composed and edited by Dr. V. Babu, Secretary-ISAS Kerala Chapter. He works as Scientific Officer in the R&D Department of Hindustan Insecticides Limited, Udyogamandal, 683501, Kerala State.

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Contents

	Page
Editor's Notes	1
Indian Analytical Science Congress	2
List of new office bearers of ISAS	3
Message from ISAS President	4
Mass Spectrometry workshop announcement	5
Analytical Sciences for Production of Reactor Grade Uranium metal by K.N. Hareendran and Dr (Smt.) S.B. Roy	6
Rare Earth Based Environmentally Benign Yellow Inorganic Pigments-Production and Characterization by M.L.P. Reddy and V. S. Vishnu	14

Editor's Note:

Welcome to ISAS News Letter Volume 1, No 1. The Bulletin of the Indian Society of Analytical Scientists, the official publication of ISAS has not been published for quite some time. It may take some more time to sort out the problems. In the meantime the newly elected executive committee of ISAS during the meeting held at Mumbai on 6th February, 2009 has decided to start the ISAS news letter to publicize the activities of ISAS and act as a communication channel between the members. On the basis of this issue of ISAS newsletter is brought out. I am thankful to the President for giving me opportunity to edit the newsletter. We plan to start "Letters to Editor Column". Members of ISAS may kindly send their comments /opinions/ suggestions, etc. to the editor by e-mail. I would like to thank all the contributors for the time and effort they have spent preparing the articles for this edition which I hope you will find both informative and interesting.

Indian Analytical Science Congress -2008



Participants of Indian Analytical Science Congress 2008 (IASC-2008) held at Munnar, Kerala State during November 21-23, 2008

The Indian Analytical Science Congress-2008 was held at Hotel, Tea County, Munnar, Kerala State during November 21-23, 2008. The congress was inaugurated by Dr James Jacob, Director, Rubber Research Institute of India, Kottayam, Kerala. The inaugural meeting was presided over by Dr P.K. Jaiswal, President, ISAS. Dr Raghaw Saran, Secretary-ISAS, Shri Devaraj Aiyer, Vice President-ISAS, Dr V.R.Nair, Chairman-ISAS - Kerala chapter and Mrs Hema Nayar, Treasurer -ISAS - Kerala Chapter also spoke on the occasion. The theme of the congress was ,”Analytical Sciences for Sustainable Development”. It was attended by more than 150 delegates from all over India. Ninety one papers were presented in the conference. Prizes were given to students who presented the best posters. The best poster paper award was given to Ms Bolie Therattil of CUSAT, Kochi and the second best poster paper was given to Mr Mujeebu Rehman of CWRDM, Calicut. Along with the congress an exhibition of analytical equipments by leading analytical equipment suppliers in the country was also organized. The next Indian Analytical Science Congress will be held at Nasik during November /December 2009.



IASC-2008 inaugurated by Dr James Jacob, Director Rubber Research Institute of India, Kottayam, Kerala

New Office bearers of ISAS

The following were elected as the office bearers of ISAS central body for the period 2008-11

President	Dr V.R.Nair
Vice Presidents	Dr P.K.Jaiswal
..	Dr Raghaw Saran
..	Prof Sriman Narayan
..	Dr N.K.Pillai
Hon.Secretary	Dr Abdul Rashid
Joint Secretary	Dr G.P.Sharma
	Shri Nagpure
Treasurer	Dr P.Unnikrishnan
Joint Treasurer	Shri M.N Nagarnaik
Executive Committee members	1.Smt Bencey Cyriac 2. Smt. Usha Nathan

	<ol style="list-style-type: none">3. Prof S. Sriman4. Smt K.Bhubaneshwari5. Shri Nitish Chakraborty6. Shri B. Krishnamacharyulu7. Dr. J. Christopher
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Message from New President

First of all I thank members of ISAS for electing me as President of the society for the period 2008-11. I am honored by your selection and very pleased to have the opportunity to work with you in a number of timely and important areas. Through this message I want to share with you, and in this way let you know of a group of initiatives that I think are very important to the future of the society. During this period myself and other members of the executive committee will be concentrating our efforts to make ISAS a highly professional and visible society. ISAS was established in 1983 with the goal of promoting Analytical Science in India. With 13 chapters spread all over India and having more than two thousand life members ISAS is a resource that brings together the best of minds in our country. It is a miracle that such a small scientific association could not only maintain its ground over more than 25 years but also succeed in setting new goals and follow carefully selected goals. ISAS could also grow and prosper in spite of being faced with an increasing competition with many other, often much larger, organizations. The major reasons for this vitality are the thematic scope of activities of the ISAS and the joint efforts of its members to make these activities a success and to give them a substantial degree of publicity.

Analytical Science plays a vital role in the development in our country. It is also one of the most important forces behind the booming high-tech industry in our country. Environmental pollution, energy deficiency and food shortage problems in India would require the devotion and assistance from analytical scientists. Therefore, strengthening the communication and interaction among ISAS members with the rest of the world in order to help solving the above challenges should be one of the highest priorities of ISAS in the future. To achieve this objective ISAS has initiated several programmes.

In the past ISAS has organized numerous conferences/ symposia/ seminars/workshops in different parts of India providing platforms to its members for exchanging ideas and enabling them to keep abreast of the latest developments in analytical science. From 2007 onwards ISAS is organizing Indian Analytical Science Congress. The last congress organized at Munnar, Kerala with the theme, "Analytical Sciences for Sustainable Development", was a big success because of the remarkably high attendance and excellent quality of the scientific program. The next

analytical science congress will be organized at Nasik during November/December 2009 . It has also been decided to organize an International Conference on Analytical Science during 2010. These events are expected to give a big boost to the discipline of Analytical Science in our country.

During the three year term the new executive committee will focus on the following areas: a) enhancement of member services(b) promotion of collaboration between industry and academia(c)collaboration with other technical organizations and societies with similar objectives(d)publication of an e-journal and (e) upgrading of ISAS website. Suggestions from members of ISAS are invited .

In the coming years we plan to increase the membership of ISAS and also start new chapters in various parts of India where Chapters of ISAS are not existing at present. New members and chapters will help to broaden and strengthen the basis of activities of ISAS .I would like to request all members for their support in all the activities of ISAS. By integrating the knowledge and wisdom of each individual member we can improve ISAS further enabling it to respond positively to the demands of the nation and society. The support and cooperation of each member of ISAS will be appreciated to achieve the above objectives.

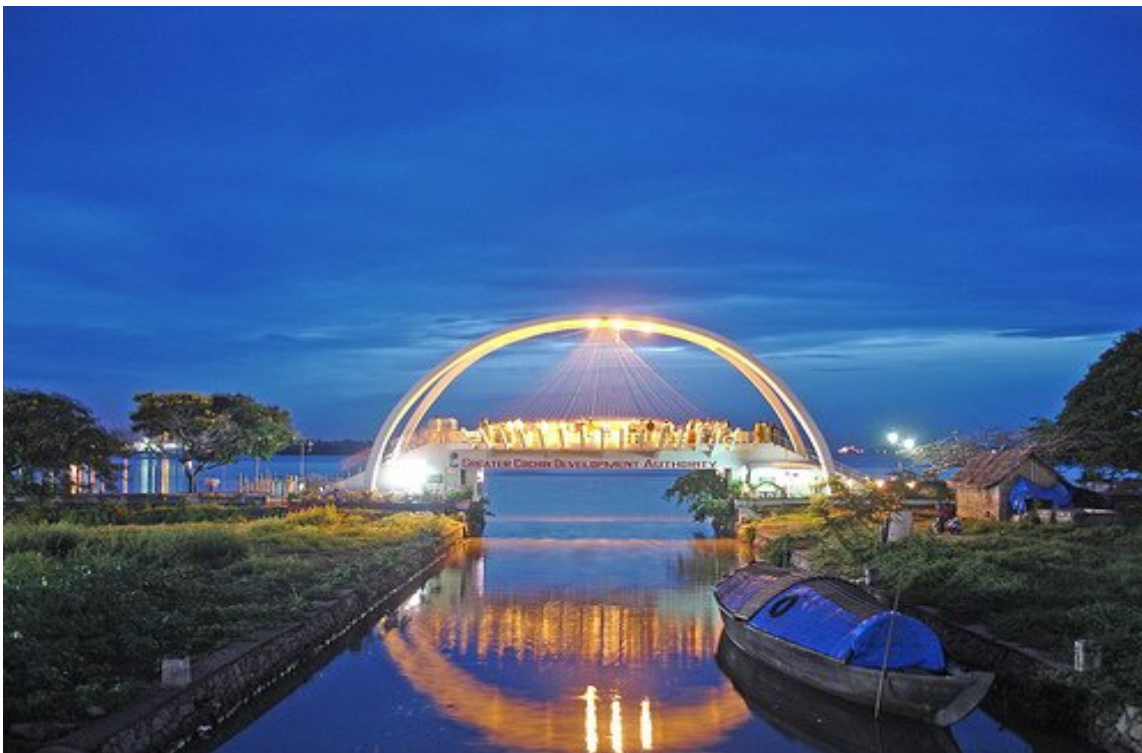
Thank you

Dr V.R.Nair

President-ISAS

Workshop on Mass Spectrometry and Related Hyphenated Techniques in Analytical Science

ISAS is organizing an one day workshop on Mass Spectrometry and Related Hyphenated Techniques in Analytical Science at Hotel Bolghatty Palace, Bolghatty Island, Cochin on April 25,2009. Experts in the area of Mass spectrometry and hyphenated techniques are participating in the workshop and delivering lectures. For details please see ISAS website www.isasinternational.com. Make your plans and join analytical scientists all over India participating in the workshop. This workshop offers junior and senior analytical scientists an opportunity and forum to exchange ideas and experience.



Photograph of Rainbow Bridge near Bolghatty Palace Hotel, Cochin, the venue for the workshop on Mass Spectrometry

ANALYTICAL SCIENCES FOR PRODUCTION OF REACTOR GRADE URANIUM METAL

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1.0 Abstract

Uranium Extraction Division (UED) has been engaged in the production and committed supply of nuclear grade uranium metal ingots for the fabrication of fuel rods for research reactors at Trombay. Nuclear grade uranium metal has stringent specifications with respect to metallic and nonmetallic impurities. Chemical quality assurance of the raw materials, uranium metal and quality control of the production process to achieve sustainable production of this important metal is a challenging job. UED has a well equipped Quality Control Laboratory capable of carrying out this job. The production of uranium metal involves operations such as dissolution of concentrate/recycle material in nitric acid, purification of uranyl nitrate by solvent extraction using TBP, ammonium diuranate (ADU) precipitation, conversion of ADU to UO_3 , reduction of UO_3 to UO_2 , conversion of UO_2 to UF_4 and finally reduction of UF_4 to U metal by magnesium. Naturally the requirement of analysis in terms of variety of

samples and concentration range is wide. Major raw materials requiring analysis are uranium concentrate from various scrap sources, ADU from IREL, magnesium metal, TBP and graphite. Uranyl nitrate solution having concentrations ranging from ppm to molar, UO_3 and UF_4 are the main process samples required to be analyzed for process control. Metal grade UF_4 requires determination of H_2O , HF, UO_2 and UO_2F_2 . Finally the uranium metal ingot is analyzed for twenty trace level impurities.

Quality control laboratory has been employing both classical methods like volumetry and gravimetry as well as state-of-the-art analytical instruments such as ICPAES, AAS, EDXRF to name a few. Since a large number of plant samples require uranium determination, UED has recently installed an EDXRF system capable of handling both liquid and solid samples. This method apart from being non-destructive produces reliable results quickly which helps in the down stream processing in the plant. Generation of complex analytical waste also has been avoided. However, volumetric determination of uranium, due to its high precision, is still being practiced for nuclear material accounting analysis. Determination of trace level impurities is also required in ADUC, UO_3 , magnesium, graphite and uranium metal. For achieving this objective a high resolution sequential Inductively Coupled Plasma Atomic Emission Spectrometer has been used. Determination of carbon in uranium is carried out by its conversion to CO_2 and measurement by an IR detector using an automatic Carbon-Sulphur Analyser. Disposal of plant effluents must meet the regulatory limits set by MPCB. The analysis of effluents including nitrate and fluoride is also carried out regularly. In addition to chemical analysis, physical characterization of raw materials and process samples is also carried out.

2.0 Introduction

Natural uranium metal is used as the fuel in Indian research reactors, CIRUS and DHRUVA. Uranium Extraction Division (UED) of Bhabha Atomic Research Centre (BARC) has been given the mandate of producing reactor grade uranium metal for fuel fabrication for these reactors. Reactor grade uranium metal has stringent specifications with respect to a number of metallic and nonmetallic impurities as these impurities have a direct bearing on the performance of the fuel in the reactor. UED will be completing 50 years of successful and uninterrupted production of this important material in January, 2009. Analytical chemistry has played a pivotal role in the development of the process flow sheet for production of uranium metal and also in the successful operation of the production facility during the last fifty years. This paper reviews the role of analytical sciences in the production of reactor grade uranium metal.

3.0 Production of Uranium Metal

The plant process flow sheet is given in Fig.1. The starting materials for production of uranium metal is either magnesium diuranate (MDU) or recycle material from the plant as well as fuel fabrication facility, which is dissolved in nitric acid to obtain an impure uranyl nitrate solution. The purification of the impure uranyl nitrate is carried out by solvent extraction process using Tri-n-Butyl Phosphate (TBP) diluted with kerosene. Ammonium diuranate (ADU) is precipitated from the pure uranyl nitrate thus obtained, which is calcined to obtain UO_3 . UO_3 is reduced to UO_2 using hydrogen. UO_2 is converted into UF_4 by reacting with anhydrous HF. Finally, UF_4 is reduced to uranium

Process Flow Sheet for the Production of Uranium Metal Ingots

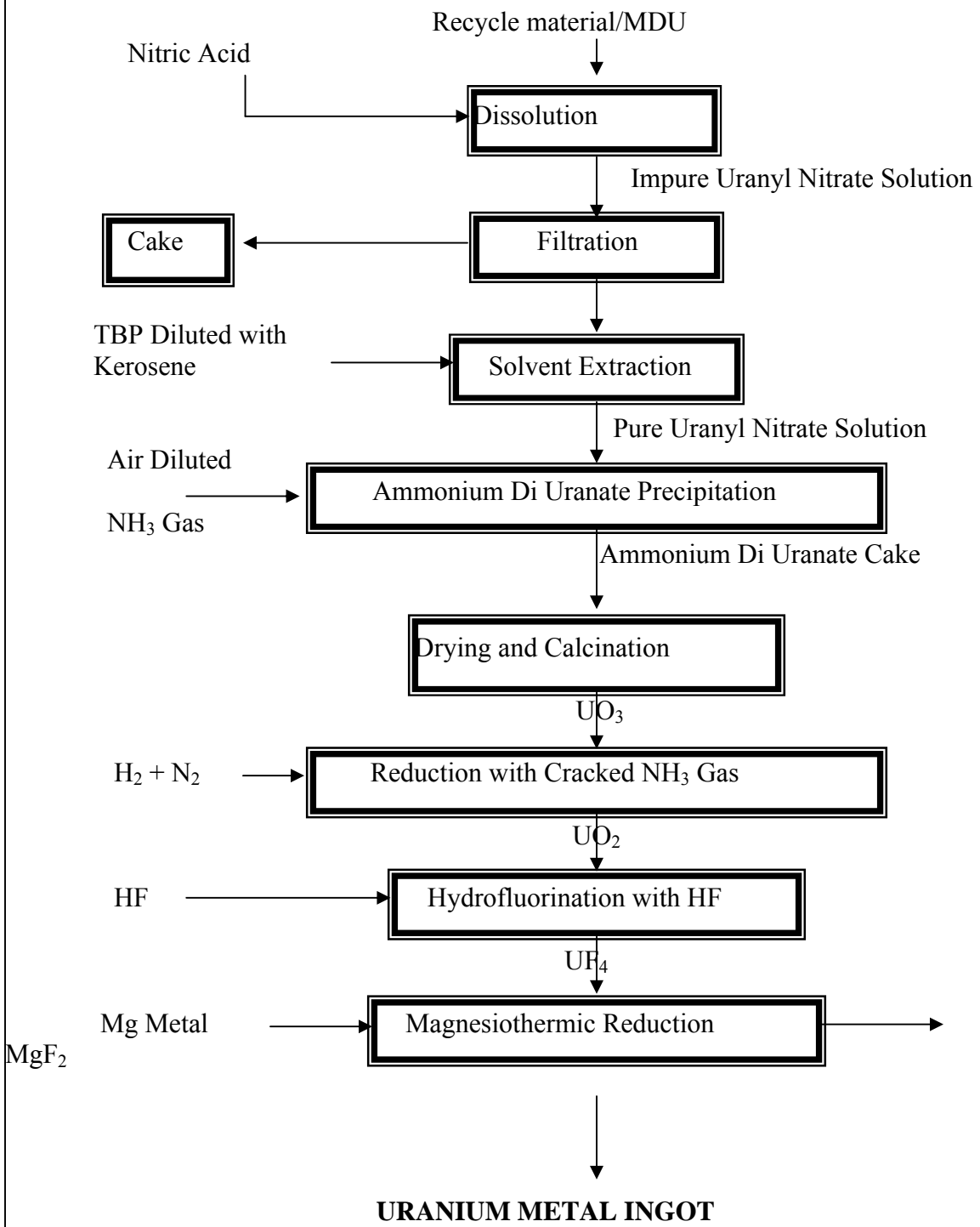


Fig - 1

metal by reduction with magnesium. Magnesium fluoride is obtained as slag which is processed to recover uranium and also to use as liner material in the bomb reactor used for carrying out magnesiothermic reduction of UF_4 . The plant also generates waste streams containing nitrate and fluoride which are treated and disposed.

The specification for the reactor grade uranium metal is given in Table-1. It is obvious that in order to assure the quality of the final product metal, it is imperative that the quality control program for the production of uranium metal should encompass raw materials, process streams, final product and the waste streams. UED has a Quality Control Laboratory equipped with a gamut of analytical techniques ranging from classical methods like gravimetry, volumetry etc and also the state-of-the-art analytical instruments like ICPAES, AAS, EDXRF

3.1 Sampling Methodology

Reliability and accuracy of analytical results critically depend on the representative nature of the laboratory sample to the bulk [1]. A well structured sampling procedure based on international practices and ones own experience will be sufficient to produce representative samples. UED handles powder, liquid and metal ingots and different sampling procedures are adopted to obtain representative samples. Powder materials such as ADUC, UO_3 , UF_4 and magnesium chips, random sampling is carried out from each drum for every batch. These samples are homogenized by mixing. In the case of solutions, samples are drawn while the contents of the container/tank are kept agitated. In the case of magnesium metal ingots, samples are drawn by drilling at selected locations. Uranium metal ingots are also samples by drilling at four diagonally opposite locations.

Most of the solid samples require acid dissolution prior to their analysis by either wet chemical or instrumental methods. Nitric acid dissolution is sufficient for samples from the plant. However, refractory materials are dissolved using a microwave assisted sample digester. Most of the instrumental methods of analysis suffer from matrix interference resulting in deterioration of their detection limits. In order to achieve lower detection limits as well as to avoid matrix effects in instrumental analysis, a matrix removal step becomes necessary. Solvent extraction is practiced in our laboratory to achieve this objective.

Table-1

Specification for reactor grade uranium metal

Sr.No	Impurity element	Maximum limit, ppm
1	Aluminium	100
2	Boron	0.12
3	Cadmium	0.12
4	Carbon	800
5	Cerium	0.2

6	Chromium	65
7	Cobalt	1.2
8	Dysprosium	0.1
9	Erbium	0.1
10	Europium	0.04
11	Gadolinium	0.04
12	Iron	150
13	Magnesium	25
14	Manganese	25
15	Nickel	100
16	Nitrogen	100
17	Samarium	0.1
18	Thorium	10
19	Ytterbium	0.1
20	Yttrium	0.1

3.2 Analysis of Raw Materials

Production of uranium metal necessitates regular procurement of a number of raw materials like ADU, nitric acid, TBP, magnesium and graphite. Procurement of raw materials of required purity is the first step towards achieving production of uranium metal meeting nuclear specifications. It is important to develop reliable sources of supply of these raw materials with adequate quality control facilities, nevertheless final acceptance of these materials will have to be approved by us based on the analysis done in our laboratory. Raw materials used for uranium metal production and the constituents to be analysed along with the analytical methods are given in Table-2.

Table-2

Analysis of raw materials

Raw material	Analysed for	Analytical method
ADU	Trace level metallic impurities	ICPAES
Nitric acid	% assay	Volumetry
TBP	% assay, H ₃ PO ₄	Volumetry
Graphite	Trace level metallic impurities	AAS, ICPAES
Magnesium	Trace level metallic impurities MgO	ICPAES Gravimetry

Table-3

Analysis of process control samples

Process Step	Samples analysed	Process control parameter	Analytical Method
Dissolution	UO ₂ (NO ₃) ₂ solution	U	Volumetry/EDXRF
		Free acidity	Volumetry
Solvent Extraction	Feed	U	Volumetry/EDXRF
		Free acidity	Volumetry
	Extract	U	Volumetry
	Scrubbed extract	U	Volumetry
	Scrub raffinate	U	Volumetry/EDXRF
	Raffinate	U	EDXRF/UV-Visible
	Strip solution	U	Volumetry/EDXRF
		Trace metallic impurities	ICPAES
	Barren organic	U	Volumetry
TBP		Volumetry	
DBP		Volumetry	
ADU Precipitation	ADU	Moisture	Gravimetry
		Particle Size	Laser Diffraction
	ADU Filtrate	Nitrate	Kjeldhal
Calcination	UO ₃	O/U ratio	Gravimetry
		Particle Size	Laser Diffraction
		Trace metallic impurities	ICPAES
Hydrofluorination	UF ₄	U-oxide	Gravimetry
		UO ₂ F ₂	UV-Vis Spectrophotometry
		Moisture	Gravimetry
		Free acid	Volumetry
Magnesiothermy	Slag	U	EDXRF/UV-Visible
		Fe	UV-Vis Spectrophotometry
		Size analysis	Sieve shaker

3.3 Process Control Analysis

Uranium metal production process requires close monitoring of various chemical and physical parameters for process control. Sampling points are provided in the process flow sheet to monitor the process status. Samples are drawn at regular intervals from various points and are analysed. These analyses provide the production team information about the deviations in the process parameters and help them take corrective actions.

Table-3 gives the details of the process control samples analysed along with the analytical techniques employed

3.4 Quality Assurance of Uranium Metal

Reactor grade uranium metal has very stringent specifications as given in Table-1. Determination of all these impurities is carried out using techniques such as Inductively Coupled Plasma Atomic Emission Spectrometer (ICPAES) and a Flame Atomic Absorption Spectrophotometer (FAAS) and UV-Visible spectrophotometry.

3.5 Analysis of Waste Streams

During the production process two waste streams containing high concentrations of nitrate are generated which are disposed as per the MPCB norms. Analysis of nitrate is carried out by Kjeldhal distillation method followed by titrimetry of the ammonia distilled out. Fluoride in plant effluents is determined using a fluoride selective electrode

4.0 Analytical Techniques in Quality Control Laboratory

Quality Control Laboratory of UED employs a number of analytical techniques for analyses of samples from the plant. The laboratory houses many modern analytical equipment. These include ICPAES, FAAS, EDXRF, UV-Visible spectrophotometers, Laser diffraction particle size analyzer, CS analyzer, moisture balances and Ion meters. Different analytical techniques used for determination of various constituents in samples from plant are briefly described below.

4.1 Uranium Determination

Uranium determination is carried out by four different methods depending upon the concentration and purity of the sample.

Gravimetry: This method is based on the direct conversion of uranyl nitrate or ADU to U_3O_8 . However, this method has limited application as the samples should be highly pure substances.

UV-Visible Spectrophotometry: Measurement of absorbance of the yellow coloured uranium-thiocyanate complex with an absorption maxima at 375nm is utilized in spectrophotometric determination. Though the method has limited sensitivity, for analyzing plant solutions containing various impurities, this method is found to be more suitable as selectivity is achieved using solvent extraction.

Volumetry: Volumetry is based on redox reactions involving different oxidation states of uranium. U(VI) is reduced to U(IV) with Fe(II) in $Con.H_3PO_4$ medium and the excess Fe(II) is oxidized to Fe(III) with nitric acid. U(IV) is titrated with standard potassium dichromate solution using a potentiometric or a visual indicator end point. This method is used for determination of uranium in process solutions and also in samples analysed for nuclear material accounting purpose as the method has high precision [2,3].

Energy Dispersive X Ray Fluorescence Spectrometry (EDXRF): Recently UED has installed an EDXRF spectrometer for analysis of uranium in plant process samples. This method is non-destructive and offers precision sufficient for process sample analysis.

This method has resulted in faster analysis and feed back to plant. However, volumetry is still being used if the analysis demands high precision [4].

4.2 Determination of Free Acidity

Determination of free acidity is required in almost all aqueous samples from the plant. Free acidity determination is carried out by alkalimetry after complexation of uranium with fluoride.

4.3 Determination of Moisture Content

Moisture content determination is required in ADU and UF₄ samples and is carried out using automatic moisture balances. Earlier, oven drying method was in use, which requires at least 4 hours to complete analysis of a sample. The current method is very fast and requires less manpower and also speed up production process.

4.4 Determination of Particle Size

Particle size determination of ADU, UO₃ and UF₄ is regularly carried out using a Laser Diffraction Particle Size Analyser. Particle size is an important physical parameter from downstream processing point of view of these intermediates.

4.5 Determination of Trace Metallic Impurities

Trace level metallic impurities are required to be determined in graphite, magnesium, pure uranyl nitrate solution obtained from Solvent Extraction operation, UO₃ and product uranium metal. To achieve this objective UED uses a high resolution Sequential ICPAES and a FAAS. ICPAES offers low detection limits coupled with high precision for determination of most of the fuel specification elements except Th, C and N. However, in order to overcome the interference caused by uranium matrix, UED follows the DAE-ILCE procedure of sample preparation, in which uranium is removed by extraction with TBP-CCl₄ and TOPO-CCl₄ [5]. FAAS is employed for analysis of samples where only Cu, Fe etc are to be analysed. Though less sensitive compared to ICPAES, it is a useful technique for elements like Al, Fe, Mn, Mg, and Cr which are present in uranium metal in the analytical range of FAAS. Thorium is determined by extraction spectrophotometry using Arsenazo(III). Nitrogen is determined by Kjeldhal distillation followed by UV-Visible spectrophotometry. Carbon determination is carried out by conversion to CO₂ and its measurement by an IR detector using an automatic Carbon-Sulphur Analyser

5.0 Conclusion

Analytical chemistry plays a vital role in the production of reactor grade uranium metal. Selection of appropriate analytical techniques has helped in the rapid and accurate analyses of samples, helping production of uranium metal of quality and quantity. Though the current analytical procedures are well established, in recent times our focus has shifted to adopting instrumental techniques to replace classical methods which are man power intensive and time consuming.

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RARE EARTH BASED ENVIRONMENTALLY BENIGN YELLOW INORGANIC PIGMENTS-PREPARATION AND CHARACTERIZATION

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Inorganic pigments have been utilized by mankind since ancient times [1] and are still widely used in various applications such as paints, inks, plastics, rubbers, ceramics, paper, cosmetics, enamels and glasses [2,3]. Indeed, in the case of glasses, glazes and ceramics, there is no alternate to inorganic pigments for coloring. However, most inorganic pigments contain heavy metals that can adversely affect the environment and human health if critical levels are exceeded [4]. Thus there is a strong incentive to design new colorants based on inorganic materials to substitute for industrial pigments that are based on toxic metals. Yellow is particularly important color in the pigment industry and the consumption of the yellow exceeds that of any other colored pigments. There are various important yellow pigment families: tin vanadia yellows, praseodymium zircon, zircon vanadia yellow, cadmium yellow and lead antimonite. Among them, praseodymium yellow (ZrSiO₄:Pr) has been known as one of the environmentally benign inorganic colorants, which can be applied to paints, inks, plastics, rubbers, ceramics, enamels and glasses because of its thermal stability [5,6]. However, this pigment requires high temperature calcinations (>1273 K) for the preparation, which tends to induce particle growth of the pigment. Hence, it is difficult to apply the praseodymium yellow to paints and inks in which fine dispersion of the pigment is essential. Other yellow pigments commonly used such as Pb₂Sb₂O₇, PbCrO₄ and CdS are now being expelled from the market because of their toxicity.

The characteristics required for commercial use of pigments are: color-tone and saturation, color covering, tinting strength, brightening and brilliance ability, non-reactivity, insolubility and dispersibility [6,7]. In addition to absorbing light, their ability to scatter or reflect light also contributes to their functionality. Recently, many rare earth-based inorganic pigments have been proposed by several researchers including our group [8–11]. Among several pigments for the alternative non-toxic yellow pigments, CeO₂ and related materials have been attracted because of the opacity, low toxicity, and high

temperature stability [12–14]. The coloring mechanism is based on the charge-transfer band from O_{2p} to Ce_{4f} in the semiconducting CeO_2 . The band gap between the anionic O_{2p} valence band and the cationic Ce_{4f} conduction band can be modified by the formation of solid solutions, which introduces an additional electronic level between the valence and conduction bands. As a result, shift of the charge-transfer band is observed. This review intends in bringing out some of the recent trends in this field.

There exist a large number of inorganic pigments formulations in the state of art, in which transition metals have been employed as chromophores. In contrast, rare earths are quite sparingly used in the inorganic pigments. A notable exception is praseodymium in praseodymium zircon yellow (Dry colour Manufactures Association).

The use of praseodymium doped zirconium silicate crystals as a pigment in ceramic glazes was disclosed by C. A. Seabright in U.S. Patent No. 2,992,123, July 1961. Since that time, there have been numerous patents issued for praseodymium doped zircons for ceramic applications and now it is manufactured world wide. Stable pigment particles comprising praseodymium doped zirconium silicate particles, at least about 50 percent by volume of which range from 0.2 to 2 μm size has been disclosed in a U.S. Patent 5,316,570, May 31, 1994, which can be used for plastics and paints.

A new class of environmentally benign yellow rare earth pigments as alternatives to lead, cadmium and chromium pigments has been proposed based on cerium molybdenum oxides corresponding to the structural formulae $NaCe_{0.5}(MoO_4)$ and $Ce(MoO_4)_2$ [13]. The coloring properties of the compositions prepared by varying the Ce:Mo ratio in the presence and absence of phosphates have been evaluated. The reflectance spectra and photoacoustic spectra indicate the absorption in visible and ultraviolet regions under 500 nm, which could originate from the O_{2p} - Ce_{4f} and the O_{2p} - Mo_{3d} double charge transfer transitions, and as a result the pigments show yellow color.

New inorganic pigments based on amorphous cerium tungstate, $Ce_{1-x}M_xW_2O_8$ ($M = Zr$ or Ti , $0 \leq x \leq 0.6$), were synthesized and their color properties were characterized from the viewpoint of possible ecological inorganic pigments [14]. The $Ce_{1-x}M_xW_2O_8$ materials absorb the visible and the ultraviolet light under 500 nm efficiently, which is originated in the O_{2p} - Ce_{4f} and the O_{2p} - W_{5d} double charge transfer transitions, and, as a result, the pigments can show a brilliant yellow color (Fig. 1). The optical absorption edge wavelength of these pigments depends on the Zr or Ti content, and the effective yellow hue was observed at $x = 0.2$ for both pigments. The color properties of these pigments suggest that they have a potential to be applied as a satisfactory pigment for paints. Furthermore, these pigments can be prepared by a simple co-precipitation method. They are inert and safe and do not produce side effects in the human body because they are composed of non-toxic and safe elements.

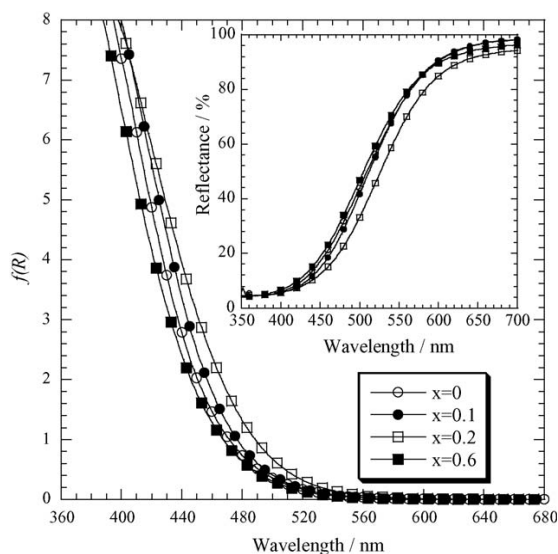


Fig. 1 Absorbance spectra of the amorphous $Ce_{1-x}Zr_xW_2O_8$ pigments. The corresponding reflectance spectra are also depicted as the inset

$Ce_{1-x}Zr_xBi_yO_{2-y/2}$ solid solutions were synthesized as new inorganic yellow pigments and their color properties have been investigated as possible ecological materials [15]. Although the optical absorption edge of the $Ce_{1-x}Zr_xBi_yO_{2-y/2}$ pigments depends on their composition, all samples absorb the ultraviolet and the visible light under 500 nm efficiently. As a result, the pigments show a brilliant yellow color, and the most effective yellow hue was obtained at $x = 0.37$ and $y = 0.20$. The importance of the presence of Bi^{3+} in the CeO_2 - ZrO_2 lattice has been elucidated by comparing the color of $Ce_{0.43}Zr_{0.37}Bi_{0.20}O_{1.9}$ with that of $Ce_{0.43}Zr_{0.37}La_{0.20}O_{1.9}$. The optical properties of the $Ce_{1-x}Zr_xBi_yO_{2-y/2}$ solid solutions suggests that they have a potential to be alternative yellow colorants for paints, inks, plastics, and ceramics.

Novel environmentally benign rare earth pigments of general formula $Pr_{2-x}Ca_xMo_2O_{9-\delta}$ (x ranges from 0 to 1.0) displaying colors ranging from green to yellow were synthesized by traditional solid-state route, as alternatives to lead, cadmium and chromium colorants [16]. The products were characterized by X-ray powder diffraction, UV-vis spectroscopy and CIE- $L^*a^*b^*$ 1976 color scales. Fig. 2 shows the X-ray diffraction patterns for $Pr_{2-x}Ca_xMo_2O_{9-\delta}$ with different doping content of Ca, where $x = 0, 0.10$ and 0.20 , respectively. The XRD pattern of the pure $Pr_2Mo_2O_9$ sample can be indexed very well as a cubic structure of $P213$ with a lattice constant of 0.7068 nm [17,18]. The XRD patterns observed for the compounds with Ca doped up to 10% were similar except minor variations (0.7060 nm for $Pr_{1.9}Ca_{0.1}Mo_2O_{9-\delta}$ and 0.7058 nm for $Pr_{1.8}Ca_{0.2}Mo_2O_{9-\delta}$) in lattice constants as compared to that of the Ca-free sample. Since Ca^{2+} (ionic radius: 0.099 nm) is slightly smaller in size than Pr^{3+} (ionic radius 0.112 nm) and in addition, the substitution of a lower valence ion in the Pr^{3+} sites leads to creation of O^{2-} vacancies, the cell volume lowers with increasing Ca content [17,18]. On the other hand, with the increase of Ca doping in $Pr_{2-x}Ca_xMo_2O_{9-\delta}$ ($x = 0.4$ to 1.0) beyond 10%, structural transformation from cubic to monoclinic fergusonite-type has been noticed from the XRD patterns of the pigment samples given in Fig. 2. Further, some minor peaks appeared in the XRD patterns when the Ca concentration is greater than 10% can be indexed to $CaMoO_4$.

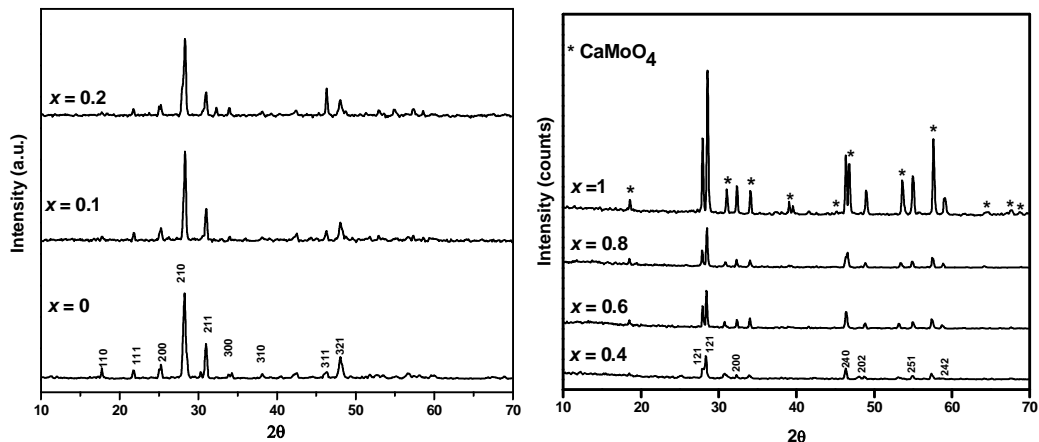


Fig. 2 XRD patterns of the $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ pigments.

The effect of calcium doping on the optical properties of $\text{Pr}_2\text{Mo}_2\text{O}_9$ based pigments was analyzed from the diffuse reflectance spectra (Fig. 3).

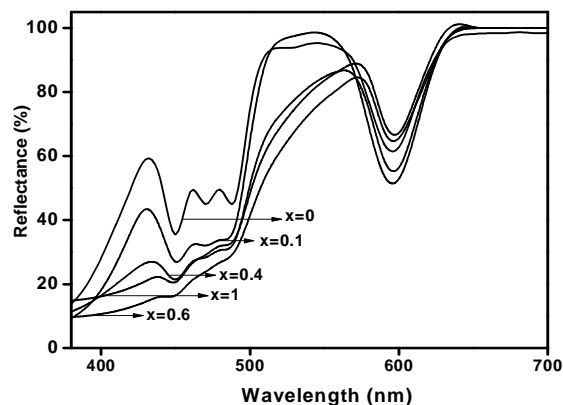


Fig. 3 Reflectance spectra of the $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ ($x = 0, 0.1$ to 1.0) pigments

In the reflectance spectra of the colorants, several bands in the visible region have been observed and can be assigned to the electronic transitions between $4f^2 \rightarrow 4f^1 5d^1$ states of Pr^{3+} . The bands in the region 440-490 (blue) and 590-625 nm (red), can be assigned based on the energy levels $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^3\text{H}_4 \rightarrow ^3\text{P}_1$, $^3\text{H}_4 \rightarrow ^3\text{P}_0$ (upper) and $^3\text{H}_4 \rightarrow ^1\text{D}_2$ and $^3\text{H}_6 \rightarrow ^3\text{P}_0$ (lower), respectively. Weak absorptions in the blue region and strong absorptions in the red region can be observed from the reflectance spectrum of the Ca-free $\text{Pr}_2\text{Mo}_2\text{O}_9$. Thus the pigment displays green color, since red is complementary color to green. On the other hand, with increasing doping of calcium into the matrix of $\text{Pr}_2\text{Mo}_2\text{O}_9$, strong absorptions in the blue region can be noticed with simultaneous weakening of the absorptions in the red region. Thus the color of the pigment gently changes from green to yellow with increasing calcium concentration, since blue is complementary color to yellow. It can be seen that the band gap of the $\text{Pr}_2\text{Mo}_2\text{O}_9$ (2.44 eV) decreases with progressive doping of calcium for praseodymium (2.23 eV for $\text{PrCaMo}_2\text{O}_{9-\delta}$). The coloring mechanism is based on the strong absorptions of the pigments in the blue and red regions due to electronic transitions between $4f^2 \rightarrow 4f^1 5d^1$ states and also due to $\text{O}_{2p} \rightarrow \text{Mo}_{3d}$ charge transfer transition. The color coordinates of the pigment $\text{Pr}_{1.4}\text{Ca}_{0.6}\text{Mo}_2\text{O}_{9-\delta}$ ($L^* = 81.53$, $a^* = -9.01$, $b^* = 59.95$), especially yellow hue

was found to be higher than that of the commercially available pigment ($L^* = 89.93$, $a^* = -3.49$, $b^* = 43.34$) Zircon Yellow (Zircon 1561: (Zr,Pr)SiO₄ of M/s Kawamura Chemicals, Japan). The designed pigments consist of non-toxic elements and further found to be thermally and chemically stable. The yellow–green pigments were found to be interesting alternatives to existing toxic pigments for coloration of plastics.

On the basis of the inductive effect as a guiding principle, cerium thiosilicates as potential yellow pigments have been reported [19]. The differences in the yellow hue of these compounds were probed by analyzing their Ce³⁺ ion environments and calculating their electronic band structures. Ce₆Si₄S₁₇ is distinguished from Ce₂SiS₅ and Ce₄Si₃S₁₂ in terms of the Ce³⁺ structural environment and the Ce³⁺ 4f¹→5d⁰ transition gap. This gap is wider for Ce₆Si₄S₁₇ than for Ce₂SiS₅ and Ce₄Si₃S₁₂ (i.e., 2.51 vs. ~2.36 eV), and Ce₆Si₄S₁₇ exhibits room-temperature luminescence whereas Ce₂SiS₅ and Ce₄Si₃S₁₂ do not. Ce₄Si₃S₁₂ and Ce₆Si₄S₁₇ possess chromatic properties similar to those found for industrial pigments such as PbCrO₄, BiVO₄, and CdS, and show thermal and chemical stabilities. Thus these compounds are potentially important yellow pigments worthy of large-scale industrial testing.

Earlier investigations also reveal that the classical toxic inorganic pigments can be replaced by solid solutions of perovskites of CaTaO₂N and LaTaON₂, which gives colors ranging from yellow to deep red [4]. Although these pigments are non-toxic and show excellent color hue, it is necessary to heat the starting materials in a flow of toxic and inflammable ammonia gas for a long time (20–60 h) to synthesize them.

U. S. Patent 6,419,735, July 16, 2002, discloses a process for the preparation of yellow samarium sesquisulphide pigment. The process consists of reacting samarium, trivalent rare earth metal, and alkali metal or alkaline earth metal compounds with a gaseous mixture of hydrogen sulphide and carbon disulphide. The compositions of the invention exhibit a strong yellow colour. However one of the shortcomings of this process is it utilizes toxic gases for the synthesis of the pigment.

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Photographs of samples of environmentally benign yellow pigments produced by the group.

