

Radiochemistry and Fuel Chemistry Programme

Chapter 5

Ensuring Research and Development Support

The concept of Anu and Panchatatva is part of ancient Hindu philosophy. The word "Anu", the smallest imaginable particle of matter, has much the same meaning that atom has in science. The atom consists of electrons and a central core called nucleus. Instability of the nucleus leads to the phenomenon of radioactivity. Study of nuclear and chemical properties of radioactive elements constitutes the branch of Nuclear and Radiochemistry that has played a pivotal role in understanding fundamentals of nuclear properties, heavy element chemistry, fuel chemistry as well as applications of radiations and radioisotopes which contributed to the growth of nuclear science and technology.

Radiochemistry programme began in the formative years of the Department of Atomic Energy and received an impetus with the commissioning of India's first reactor 'APSARA' in 1956. Construction of particle accelerators added a new dimension and enhanced the scope for research in this branch. During the last five decades, Radiochemistry and Fuel Chemistry programmes were centered around utilizing radiations and radioisotopes to unravel various nuclear and chemical processes. In addition, these also resulted in significant contributions to the plutonium utilisation programme in terms of understanding the chemistry related aspects of nuclear fuel cycle. The activities encompassed a number of research and development areas such as nuclear fission, nuclear reactions, nuclear and chemical properties of actinides, actinide spectroscopy, separation science, nuclear phenomenon for material study, chemical investigations on fuel materials, understanding thermal and thermodynamic behaviour of various fission product systems and their interactions with fuel and clad, post irradiation examination of irradiated fuels and reactor components, fuel reprocessing, developing analytical methodologies and providing chemical quality control for plutonium based nuclear fuels.



Fuel pin scanner for FBTR fuel pins

RADIOCHEMISTRY AND FUEL CHEMISTRY PROGRAMME

Ensuring Research and Development Support

Introduction

Nuclear and radiochemistry came into existence with the development of nuclear science and technology, which, in turn, had its origin in the discovery of X-rays and radioactivity. As a part of the overall developmental activities for research in nuclear science and technology, it became imperative to have a laboratory for carrying out research in nuclear and radiochemistry at DAE.

With the commissioning of India's first nuclear research reactor, APSARA, the nuclear and radiochemistry programme received a fillip. Necessity of establishing a good laboratory exclusively for carrying out radiochemical work was also realized at that time itself. As that was the first time that a work of this nature was to be started in the country and in view of the high technology involved in the design and operation of a Class A radioactive laboratory, Dr. Homi Bhabha sought the support of United Kingdom Atomic Energy Authority (UKAEA). Prof. G.R. Hall from Imperial College, London came to AEET to initiate the radiochemical studies and lead a team of radiochemists. A prototype Radiochemistry Laboratory was thus set up soon after the commissioning of APSARA. Over the years this laboratory was to serve as a training ground for a team of chemists, chemical engineers and metallurgists not only in handling highly radioactive substances but also for understanding chemical, technological and metallurgical aspects of these man-made elements including plutonium.



Radiochemistry Laboratory at South Site, Trombay, set up in 1958

The prototype laboratory having an active area of 375 sq.m and associated service area of 350 sq.m was fully commissioned and became operational by 1958. Very soon Dr. H.D. Sharma, a brilliant student of Prof. Glenn T. Seaborg of USA, joined the team. Dr. G.A. Welch from Harwell became Head, Radiochemistry Laboratory in 1959, after Prof. Hall returned to U.K. Other prominent radiochemists to join the team from abroad were Dr. M.V. Ramaniah, Dr. Ghosh Majumdar and Dr. C.L. Rao, a student of Prof. L. Yaffe of USA. Several scientists with rich experience of having worked in renowned nuclear and radiochemistry laboratories abroad also joined to strengthen the programme. Each of them headed a separate group with specific sub-programmes. Subsequently, this radiochemistry programme was sustained and augmented by young and enthusiastic graduates from Training School of BARC. They were responsible for setting up of the infrastructure for carrying out research in different areas of nuclear and radiochemistry. Some of them were sent abroad on deputation to laboratories in USA, Canada and Britain to gain experience in different areas of radiochemical research.

The laboratory at south site of Trombay complex had two radioactive wings equipped with six fume hoods in each wing. In addition, there were large number of beta, gamma boxes and glove boxes. There was a well equipped counting room with facilities for alpha and beta counting and gamma spectrometry with a 100 channel analyser. Radiochemistry research programme in the early years was based on the availability of APSARA reactor for nuclear and radiation chemistry studies and plutonium, protoactinium and actinium obtained from UKAEA for research on actinides. Preparation of Pu compounds for the first time and their thermal studies was indeed an exhilarating feeling and a proud moment. Subsequently a number of activities related to nuclear fission of actinides, process chemistry of actinides, spectroscopic and X-ray studies were undertaken.

The experience gained in the setting up of this laboratory was immensely useful in the design and construction of the major facilities created later for handling of highly radioactive substances. These include Fuel reprocessing plant, Radiometallurgy and Radiochemistry Laboratory at the Radio-

logical Lab., at IGCAR, Kalpakkam and Advanced Fuel Fabrication Facility at Tarapur. South Site Laboratory served as a training ground for chemists, chemical engineers and metallurgists who joined the department in early sixties for the handling of Pu. Many of these scientists/engineers were destined to lead the fuel fabrication/fuel reprocessing programmes of the department in subsequent years.

Dr. M.V. Ramaniah took over as Head, Radiochemistry Division, BARC in 1965 and was the driving force for the completion and commissioning of Radiological Laboratories at Trombay around 1969.



Dr. M.V. Ramaniah

The chemistry wing of the new complex has 14 radioactive laboratories of size 7 m x 10 m, three low active laboratories of size 6 m x 10 m, a modern counting room equipped with state-of-the-art instruments, and an alpha tight hot cell with master slave manipulators. Each laboratory room was provided with a large number of fume hoods and glove boxes, conditioned fresh air supply with 10-12 air changes, well managed liquid effluent system connecting all the laboratories and state-of-the-art health and safety devices for continuous monitoring of radioactivity. The alpha tight hot cell was commissioned for the synthesis of transplutonium elements and burn up studies.

The laboratory was equipped with a variety of modern instrumentation such as mass spectrometers, electron spin resonance (ESR) spectrometer, ultraviolet/visible spectrophotometer, thermal analyzer, x-ray diffraction (XRD) system and



Radiological Laboratories at Trombay

α and β spectrometers. With the commissioning of radiochemical facilities at Radiological Laboratories, the South Site Laboratories were dedicated for large scale research on high temperature chemistry of plutonium and other thermodynamic investigations on understanding the behaviour of fission product systems.



Calorimetric setup at BARC in the early days

With the expansion of nuclear energy in the country and following the bold decision of developing carbide fuel technology to utilize (uranium, plutonium) carbide as fuel for India's FBTR programme, research and development activities of radiochemistry programme needed augmentation, expansion and a new direction. Dr. M.V. Ramaniah, became the Group Director of newly formed Radiological Group consisting of Radiochemistry and Radiometallurgy Divisions. This helped considerably in integrating the plutonium programme dealing with fuel fabrication and chemical quality control and analysis.

With the increased and expanded Departmental work programme to further harness nuclear technology in terms of developing newer fuel fabrication routes and to cater to the plutonium utilization programme, there was a need for the establishment of a new division. Fuel Chemistry Division came into existence in 1985 with a mandate to focus on physico-chemical aspects of nuclear fuel and other fuel based R&D efforts. A number of research activities were undertaken with an express purpose of

- (i) augmenting the existing analytical methodology base for chemical quality control (CQC) of nuclear materials,
- (ii) understanding thermal and thermodynamic behaviour of various fission product systems and their interactions with fuel and clad,
- (iii) developing new analytical techniques for understanding the ageing management of nuclear reactor components particularly coolant channel of PHWRs,
- (iv) carrying out post-irradiation examination of nuclear fuels for burn-up as well as fission gas release, and
- (v) augmenting the database for nuclear properties of actinides.

During this period studies in nuclear fission expanded into other aspects of nuclear science namely angular momentum distribution and nuclear spectroscopy. Various non-destructive assay technique for measuring fissile materials have also been developed.

With the commissioning of VECC at Kolkata and Pelletron Accelerator at TIFR, Colaba, Mumbai, the research in nuclear chemistry has received an impetus. A beginning was made to develop nuclear probes. Starting from the Seventh Five Year Plan, the research activities were given further boost with the establishment of additional laboratories for demonstration of sol-gel technology for nuclear fuel fabrication, a pilot sol-gel fabrication facility at Tarapur, high temperature instrumentation for characterization of nuclear fuel materials, and augmentation of newer sophisticated multi-elemental analysis techniques for chemical quality control programme.

Decade of Expansion

During the Ninth Five Year Plan, two important projects were initiated to cater to the needs of enhanced plutonium utilization in nuclear energy programme. These were aimed at establishing facilities for plutonium utilization and developing alternate methodologies for processing, analysis and characterization. Augmentation of multi-elemental analysis techniques for chemical quality control programme, facilities for nuclear chemistry, actinide chemistry and analytical spectroscopy of actinides witnessed alround growth.

Further, in the Tenth Five Year Plan, work on physico-chemical and analytical aspects of Thorium based fuels was initiated to cater to the utilization of thorium based fuel technology in the future nuclear energy programme of India.

During these five decades, apart from mastering the basic radiochemical aspects of actinides particularly plutonium, re-search and development activities carried out resulted in a thorough understanding of analytical, physico-chemical behaviour, and thermodynamics of nuclear fuel materials, fission product systems and other nuclear materials. Faster, precise and accurate analytical methodologies for complete chemical characterization of materials using conventional to sophisticated analytical instrumentation were developed. Nuclear database in terms of fission yields, g-ray abundance and half-lives and other nuclear spectroscopic data was augmented. Some of the important milestone contributions during the past half-century are enumerated under different categories as follow:

- (1) Nuclear Chemistry,
- (2) Actinide and Process chemistry,
- (3) CQC of nuclear materials (including fuels),
- (4) X-ray studies and Solid state chemistry including spectroscopy of actinides and analytical spectroscopy,
- (5) High temperature studies on fuel materials,
- (6) R&D activities for special materials,
- (7) Sol-gel process for nuclear and non-nuclear applications,
- (8) Mass-spectrometry,
- (9) Development of NDA techniques, and
- (10) Training and services.

Radiochemistry Programme

A saga of excellence and a pivot in the Nuclear Fuel Cycle

Work carried out in Radiochemistry discipline can be divided into (1) Nuclear Chemistry, (2) Actinide chemistry, (3) Solid state spectroscopy of actinides, and (4) Analytical. The major contributions made are as follows.

Nuclear Chemistry

Nuclear chemistry is the study of nuclear properties using chemistry as a tool. Radiochemistry is the study of chemistry using radioactivity of the element under investigation or by tagging a radioisotope of the same or another element. Areas such as Mossbauer effect, perturbed angular correlations, and muonium and positronium chemistry in which nuclear effects are used for probing the chemical properties also come under nuclear chemistry. This subject has been of great interest since the discovery of radioactivity and X-rays and got further momentum with the discovery of nuclear fission and construction of nuclear reactors.

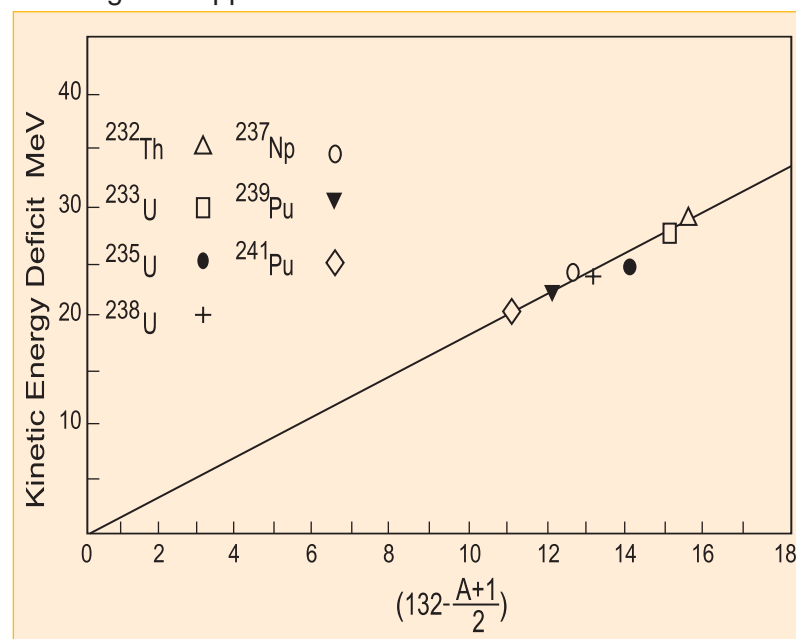
Nuclear Fission

A heavy nucleus like ^{235}U when bombarded with projectiles such as neutron and proton, forms a compound nucleus which is in excited state. If this nucleus undergoes division then it is called nuclear fission. Fission is a complex reaction involving rearrangement of a large number of nucleons. The structural rearrangement of nucleons following division of the nucleus is not unique and a host of radionuclides are produced. Additionally, in each fission an amount of 200 MeV energy and 2-3 neutrons are produced. These neutrons are utilized to initiate and sustain the nuclear chain reaction for production of energy and isotopes in nuclear reactors.

Mass and atomic numbers of fission products vary from 65-172 and 29-71 respectively. Their yields vary from 6% to 0.001%. The fission product yield distribution, as a function of mass of the product is called mass distribution. The mass distribution in the low energy fission is asymmetric with two peaks and a valley. Valley corresponds to symmetric division of the fissioning nucleus. In the early days of Radiochemistry Division, mass yield distribution in neutron induced fission of actinide isotopes like ^{232}Th , ^{227}Ac , ^{232}U , ^{245}Cm and ^{229}Th were determined radiochemically.

Expertise in radiochemical separations and radiation measurements has been utilized to measure the low yields and obtain mass yield distributions unambiguously. In addition to contributing to the nuclear data base on mass yields, two major contributions have been (i) observation of a third peak in the symmetric region in the fission of ^{232}Th , ^{227}Ac , ^{232}U and ^{229}Th and (ii) observation of shoulders in the highly asymmetric regions.

Extensive work has been carried out on the measurement of recoil ranges of fission products in neutron induced fission of ^{232}Th , ^{232}U , ^{239}Pu , ^{241}Pu and ^{245}Cm to obtain the kinetic energy distribution. One of the most striking observations was that kinetic energy of symmetric fission products was lower than that of asymmetric fission products, which was known as kinetic energy deficit (KED). Further studies demonstrated that the KED approached zero as the mass of the symmetric fission fragment approached 132.



Correlation of KED with shell structure

Around the mid seventies, a ^{252}Cf source was obtained to investigate the spontaneous fission process. During this period investigations in charge distribution were also initiated. Variation of yields in the family of isobars as a function of charge is known as charge distribution. The charge distribution studies provide information on the effects of nuclear shell and nucleon pairing on the fission process. These are particularly relevant in the low energy fission. Extensive investigations on isobaric and isotopic yield distribution studies were carried out

in the mass region of 100-105 and 130-140 in the neutron induced fission of ^{229}Th , ^{239}Pu , ^{241}Pu , ^{245}Cm and in the spontaneous fission of ^{252}Cf . Information about the dynamics of the fission process was obtained from these studies.

In the early eighties, these studies were extended to determine fission fragment angular momenta with a view to understanding the effect of collective rotational degrees of freedom and shape of the fissioning nucleus at the scission point.

One of the fascinating aspects of the process is the generation of large angular momentum in fission fragments in the nuclear fission of a nucleus having practically no angular momentum. In order to understand this phenomenon, angular momenta for a large number of fission fragments were determined radiochemically in a number of fissioning systems. These studies revealed the role of fragment nuclear structure like nuclear shells and pairing in the fragment angular momentum.

Research in nuclear fission was extended with the availability of charged particle beams at VECC, Kolkata in the early eighties and heavy ion beams at Pelletron Accelerator at Tata Institute of Fundamental Research, Mumbai. The motivation for studying the heavy ion reactions was to unfold the multiplicity of the process involved and their evolution with the variation of entrance channel parameters such as excitation energy, angular momentum and entrance channel mass asymmetry. Studies on alpha particle induced fission helped to understand the role of fissioning nucleus, its excitation energy and the influence of angular momentum on the fission process. Although studies on the distribution of mass and charge and angular momenta continued, investigations on mass resolved angular distribution were initiated in alpha as well as proton induced fission of ^{232}Th , ^{233}U , ^{237}Np , ^{241}Am and ^{240}Pu . Emerging fission products at different angles from the target are collected in a specially fabricated chamber. Mass yields corresponding to different angles of emission were obtained from off line measurements. The results showed that angular anisotropy and mass asymmetry are correlated. However, in the case of heavy ion ($Z > 2$) induced fission, conclusive evidence of correlation between angular anisotropy and mass asymmetry was not observed. In the fission of ^{232}Th induced by low Z heavy ions such as ^{10}B , ^{12}C and ^{16}O , it was observed that mass dependence of anisotropy of fission product in these systems is very different from that of alpha induced fission. Recent studies on

^{20}Ne induced fission of ^{208}Pb have shown that anisotropy is not correlated with mass asymmetry in this system.

Studies were extended to nuclear reactions to investigate nuclear reaction mechanism. Extending the periodic table is a challenge to nuclear chemists. Expertise on radiochemical separations, fast kinetics and innovative instrumentation are needed for these studies which are both experimentally demanding and intellectually challenging. A modest beginning was made at Pelletron to produce several Becquerels of heavy nuclide ^{250}Fm by the ^{16}O induced reaction of ^{238}U and radiochemical separations were deployed to isolate it. Tracer grade ^{236}Pu was produced for the first time in India using BARC-TIFR Pelletron Facility by proton induced reaction on ^{237}Np and isolated by radiochemical separations. ^{236}Pu activity is required for internal dosimetry studies for accurate assay of plutonium in biological samples.

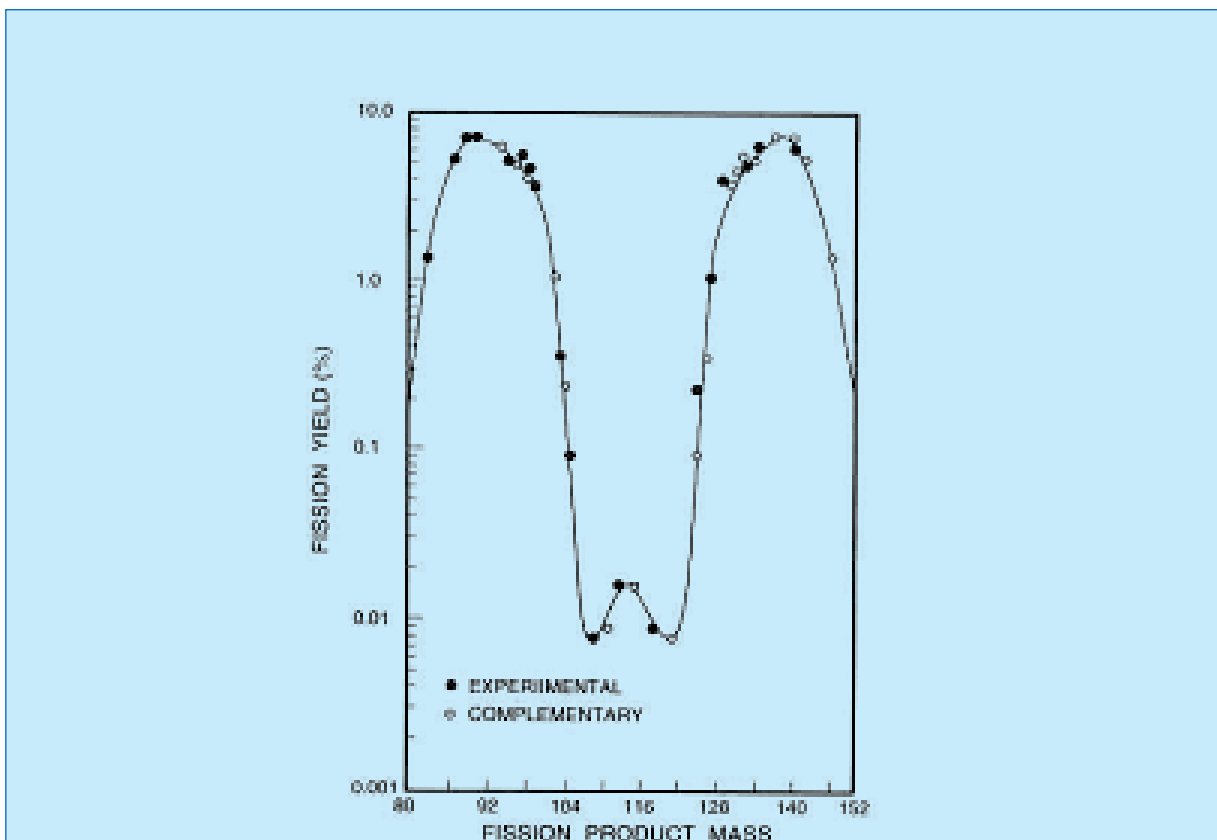
Nuclear Data

In the early eighties, studies pertaining to nuclear spectroscopy, essentially nuclear data, were initiated by determining the gamma ray abundances in the alpha decay of ^{229}Th . Expertise in radiochemical separations and nuclear measurements became handy in these studies. An alpha-spectrometric method was developed to estimate simultaneously ^{228}Th and ^{229}Th .

Recently spectroscopy data of some interesting nuclides produced in heavy ion induced nuclear reactions have been obtained. Decay scheme of $^{194}\text{Tl}^g$ was studied by radiochemically separating its parent ^{194}Pb produced in the nuclear reaction $^{181}\text{Ta} (^{19}\text{F}, 6n) ^{194}\text{Pb}$. Absolute emission probabilities of 49 prompt gamma rays from thermal neutron capture in ^{59}Co were determined by capture neutron spectroscopy. Half life of a radioisotope, in general, is invariant with the chemical environment. However, in the case of electron capture decay, there is a possibility to observe small but definite variation of half-life. This was investigated in the decay of ^7Be using different media like Al_2O_3 , Au and other metals at VECC and about 0.1% change in half life was observed depending on the medium.

Nuclear Probes

The expertise in nuclear chemistry and nuclear instrumentation has been fully exploited to develop other nuclear tech-



niques such as perturbed angular correlation (PAC) technique and positron annihilation spectroscopy (PAS). These are quite useful in understanding the different physical and chemical environment prevailing in materials at atomic scale.

The cascade gamma emission in nuclear decay has a definite angular correlation due to their electromagnetic origin. Under the influence of surrounding chemical and magnetic fields, this correlation gets perturbed and by measuring the extent of perturbation, chemical environment around the decaying probe atom can be studied. This technique was standardized and chemical environment around Hf in Hf-EDTA complexes, polymerization of Hf in aqueous solutions and after effects of β -decay, were investigated using ^{181}Hf , ^{111}In , ^{111}Ag and $^{111}\text{Cd}^m$ as the probe nuclides.

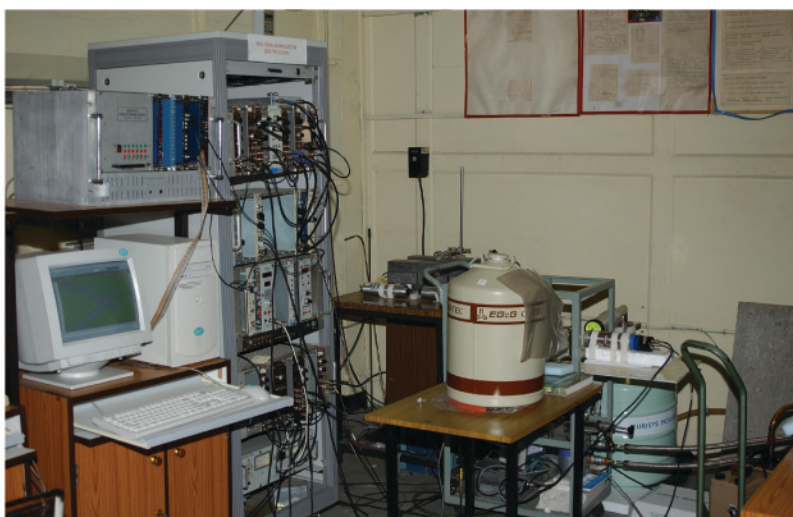
Positron annihilation spectroscopy is another nuclear technique, which has found applications in chemical and material sciences. Positron's extreme sensitivity to defects, both in terms of concentration and size is employed to probe the electronic structure of defects. Positrons, from a radioactive source, when injected into a medium, thermalise in a few picoseconds and annihilate with an electron giving two 511 keV photons emitted in opposite directions. These two photons carry information regarding electron density and electron momentum distribution in a medium. In order to extract this information various positron

techniques, viz. positron life-time spectroscopy, Doppler broadening spectroscopy and angular correlation technique were developed. These techniques were employed to study the electronic structure in a variety of materials, e.g. the microstructure of Nafion membrane (a technologically important membrane) was studied under different physical and chemical conditions. A clear dependence of the counter ion, water content and other solvent content on the free-volume structure was mapped. Temperature dependent studies revealed new molecular relaxation peaks.

Positron technique was also employed to study different porous materials. It is a powerful and *in-situ* probe for hidden surface in porous materials. Samples of metal dispersed silica, which are precursors of catalysts having industrial applications, were studied. These studies addressed understanding the positronium behavior and its localization in pores in samples with wide pore size distribution. It was shown that positronium preferentially traps in smaller pores. A state-of-the-art on applying this technique to study the MgB_2 superconductor, it was found that the electron density changes in the boron layer at the onset of superconductivity. 2-detector coincidence Doppler broadening system was developed which provided opportunity to identify the elements with which positron is annihilating in the matrix.

Nuclear Analytical Techniques

Nuclear analytical techniques (NATs) are based on utilization of certain properties of the nucleus and are associated with the phenomenon of ionizing radiations and isotopes. In NATs elemental concentrations are determined based on measurements of isotopes and/or the utilization of the processes involve in the inner shell electrons. Radiochemistry Division has contributed significantly in Neutron Activation Analysis (NAA), Prompt Gamma NAA (PGNAA) and Ion Beam Analysis (IBA) techniques.

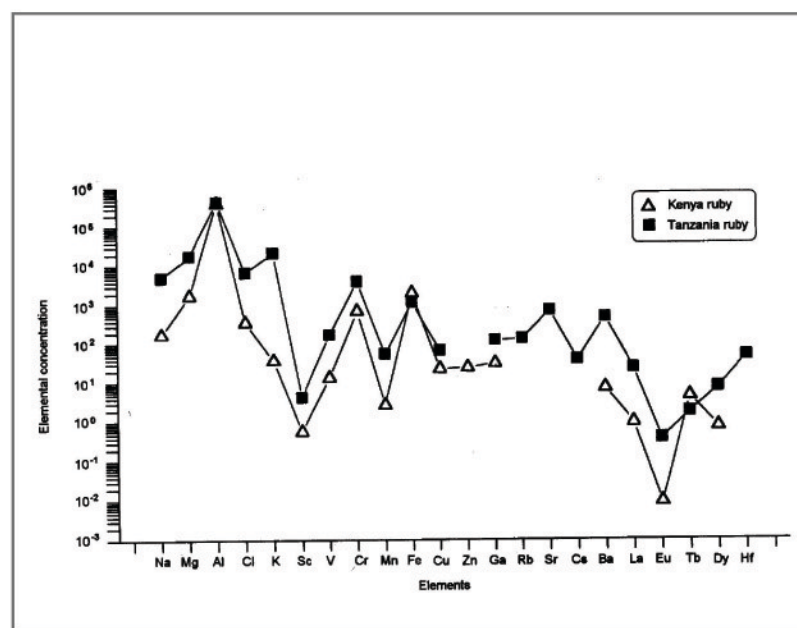


Two-Detector Coincidence Doppler Broadening Setup

Neutron Activation Analysis : NAA is a powerful analytical technique for multi element analysis. An isotope after absorbing a neutron forms, more often, a radioisotope. From the measured radioactivity of this isotope, concentration of the original isotope is determined. Use of high resolution gamma ray spectrometers enables simultaneous multielemental analysis. Elemental concentrations in a sample are determined by relative or k_0 method with detection limits ranging from nano gramme to micro gramme for many elements.

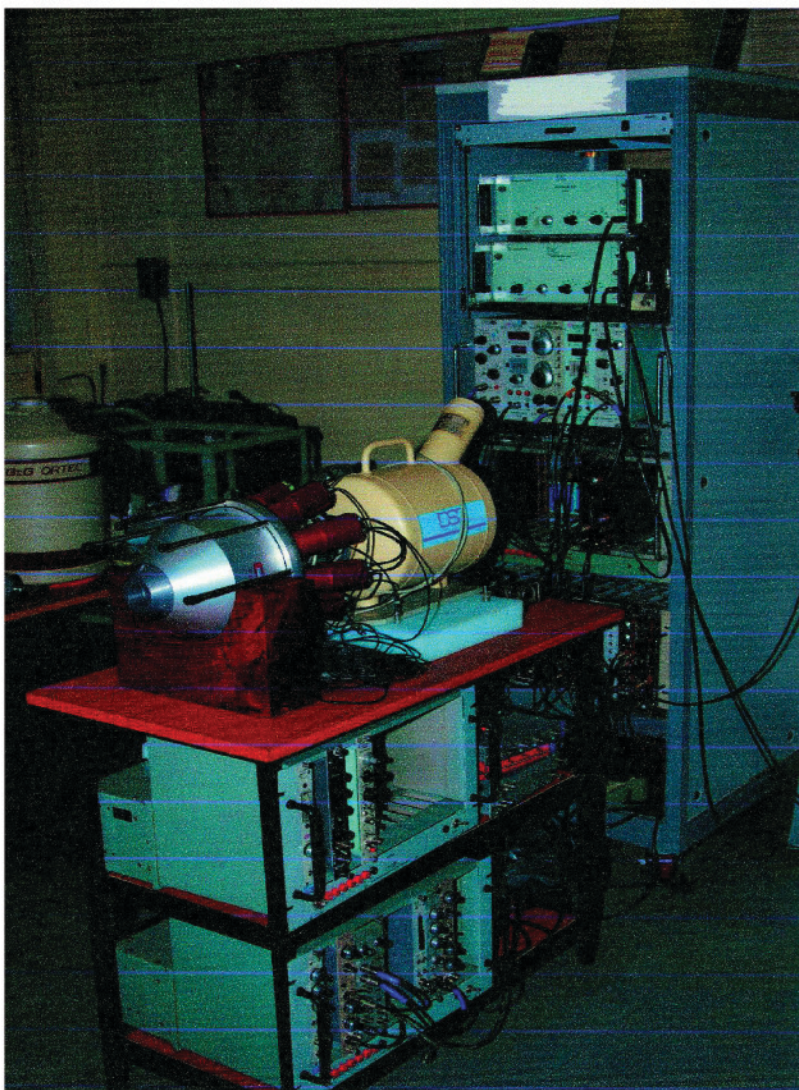
For the first time in BARC, NAA using the single comparator (k_0 NAA) was standardized and validated. It is now employed routinely for multielement analysis in varied matrices. The areas of R&D include standardization of k_0 NAA, determination k_0 factors, validation of k_0 NAA and measurement of elemental concentrations in rubies, emeralds and associated rocks, mineralisation of serpentines, ferromanganese nodules and encrustations, sediments, leaves of medicinal importance, cereals, edible leaves, soil and other plant materials. Multi

elemental profiles of natural rubys and synthetic rubys are used to find the origin of these precious stones. In addition, chemical methodologies for the determination of gold and platinum group elements (PGE) in ores, Rare Earths Elements (REEs) in minerals, derivative neutron activation analysis for determination of phosphorous and relative concentrations in large samples were developed.



Multielement analysis in rubys

Prompt gamma neutron activation analysis: PGNAA technique is complementary to offline NAA and is capable of analyzing all the elements including light elements such as H, B, C, N, P, Si and S. For the first time in BARC, a PGNAA facility was set up at DHRUVA reactor and k_0 method with ^{36}Cl as standard, was used. The prompt k_0 -factors for the elements H, B, K, Co, Cu, Ti, Ca, Cr, Ba, Cd, Hg and Gd (16 isotopes and 27 gamma lines) were determined with respect to the 1951 keV of ^{36}Cl . In view of the potential of ^{60}Co both as a comparator for k_0 standardisation as well as γ -ray standard for efficiency calibration in prompt g-ray measurement, the absolute prompt gamma ray abundances per 100 neutron capture of 49 gamma lines of ^{60}Co were determined. Elemental sensitivities for mercury, boron, samarium and cadmium were determined. The gamma ray spectrum is very complex and the energy ranges from 100 keV to 9000 keV. A Bismuth Germanium Oxide (BGO) based compton suppressed high



High resolution gamma ray spectrometer

resolution gamma ray spectrometer enabled to enhance the sensitivities.

Ion beam analysis techniques: Ion beam analysis facility for materials study was set-up at FOTIA, BARC. Rutherford back scattering was used to study the distribution of metal ions across the thickness of polymer inclusion membranes. Radiotracers were used to study diffusion of metal ions in a variety of membranes to understand the influence of ionic size and hydration radius on diffusion coefficient.

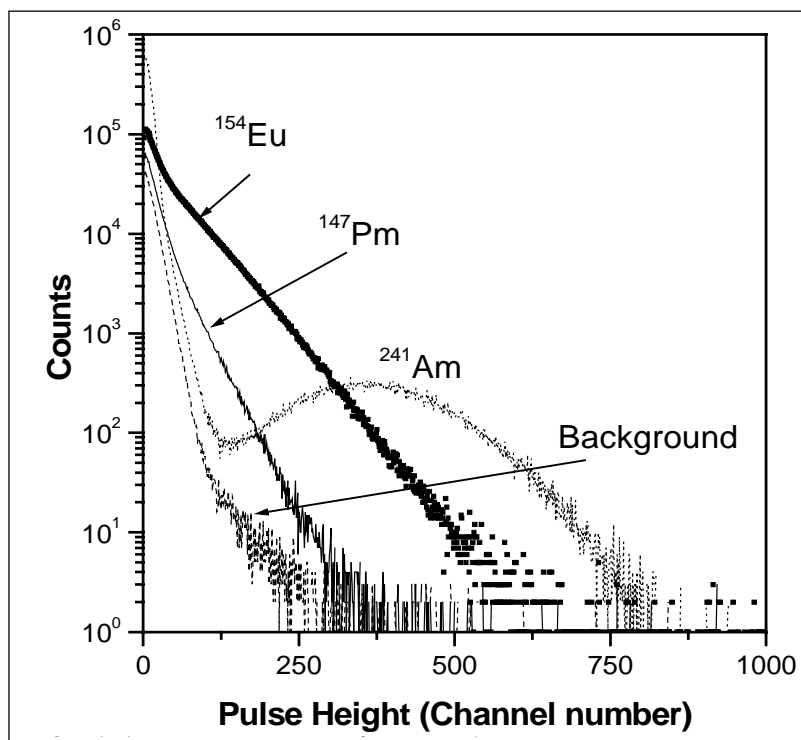
Radioisotopes in physiochemical studies : Speciation studies are important to estimate species quantitatively and to understand their interaction with other systems. Estimation often

is preceded by preconcentration. A polymer inclusion sorbent (PIS) was prepared by physical inclusion of Aliquat-336 in the matrix formed by cellulose triacetate and 2-nitrophenyl octyl ether. This sorbent was found to be stable, cost effective, efficient for preconcentration of Cr(VI) present in the aqueous samples and amenable to direct quantitation of Cr(VI) held in it by neutron activation analysis and spectrophotometry. The quantitation of Cr(VI) in PIS by spectrophotometry was carried out by developing colour directly on the PIS after reacting it with 1,5 diphenylcarbazide. The distinct colour developed on the PIS even at very low concentrations of Cr(VI) (0.4mg) suggests its possible use for field determination of Cr(VI). Retention of Cr(VI) on the PIS samples was excellent over a period of one week. Radiotracer ^{51}Cr was used to estimate the up-take of Cr(VI) and the value obtained was reproducible (88 ± 3).



Variation of colour on polymer inclusion sorbent (PIS) as a function of amount of loaded Cr(VI)

Determination of radioisotopes present at trace levels in environmental samples or any matrix needs a simple methodology that could be used at the site of sample collection. A trivalent, α emitting radionuclide selective scintillating polymer inclusion membrane (PIM) was prepared. Radioactive ^{154}Eu , ^{147}Pm and ^{241}Am were quantitatively loaded (98%) in PIM samples from aqueous solutions at pH 2.5. It was observed that β rays emitted by ^{154}Eu ($Q\beta = 1986$ keV) and ^{147}Pm ($Q\beta = 224$ keV) give different pulse heights (lower) as compared to a particles emitted by ^{241}Am . Based on this observation α - β discrimination was studied using different discriminator levels. By using appropriate discriminator level, β pulses could be effectively discriminated and at this lower level discriminator, scintillation counts due to a particles originating from the film were found to be linear with respect to the amount of activity loaded in the film. The a counting efficiency after b discrimination was found to be 40%.



Pulse Height (channel number)

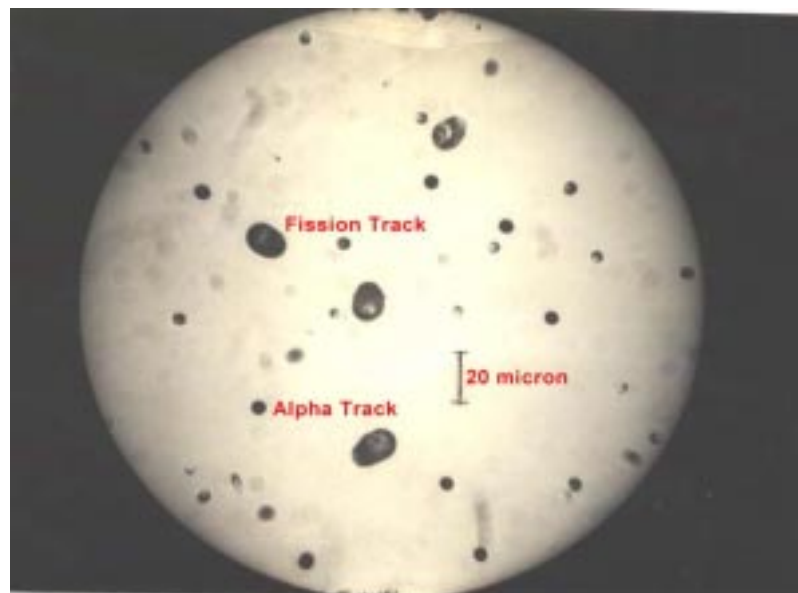
Radioactive Sources

Thin radioactive sources are needed for alpha and beta spectrometry, and for absolute disintegration rate determination of alpha and beta emitters. High resolution alpha spectrometry requires a very thin, uniform, flat and nearly mono layer source. Preparing α -sources in electrodeposition is ideal for actinide nuclides. Radiochemistry Division developed and standardised procedures for the preparation of thin α -radioactive sources from organic as well as aqueous media by electrodeposition. Many of these sources has been utilised by universities and different units of DAE.

Solid State Nuclear Track Detectors

The fact that charged particles produce invisible submicroscopic tracks in many solid insulators has led to the development of Solid State Nuclear Track Detectors (SSNTDs). It is one of the cheapest and most powerful experimental tools in the study of a number of nuclear phenomena. The shape, length and depth of these nuclear tracks is uniquely decided by the nature of the charged particle. The work on SSNTDs was initiated in the year 1967. In less than a decade, growth in the application of the family of solid state nuclear track detectors, both in size and in variety of use has been spectacular. The most important development was in the early 1980s when

SSNTDs were used for uranium exploration in many remote areas in our country. Another important milestone was the development of fission track technique for the trace level estimation of Pu and U in biological, geological and environmental samples. The technique was standardised for determination of micro Bq levels of Pu in bio-assay samples. SSNTDs were very useful in the measurement of very low events in neutron and heavy particle induced reactions on actinides and heavier lanthanides.



Photomicrograph of alpha and fission tracks in CR-39 SSNTD.

Important Milestones in Solid State Nuclear Track Detector studies

- 1980 SSNTDs used for Uranium exploration by BARC in association with AMD.
- 1985 Use of SSNTDs as neutron and gamma Dosimeter
- 1986 Track cum gamma ray spectrometric technique for the measurement of absolute yields.
- 1996 Method for trace level identification and estimation of actinides by alpha to fission cross section ratio by SSNTDs.
- 2002 Fission Track technique for ultra trace level estimation of Pu in bio-assay samples, geological and environmental samples.
- 2004 Fission track technique for determination of uranium in sea water

Non-Destructive Assay Techniques

Importance of non-destructive assay techniques in the nuclear fuel cycle was realized as early as 1967. The estimation of fissile material using high resolution gamma ray spectrometry was initiated in the early 1970's. A waste packet scanner was developed using NaI(Tl) detector and single channel analyzer during 1978 for the estimation of Pu. With the availability of 8 cc Ge(Li) detector and 4096 channel analyzer in 1978, the work on the measurement of isotopic composition of Pu by gamma ray spectrometry was initiated. Later, with the availability of 2 cc HPGe detector in 1980's the method was well established. Around the same period a hull waste monitor was set up at PREFRE Tarapur, based on the gamma spectrometric assay of fission products in the hull, using NaI(Tl) detector and analyzer assembly. A modified version of the same using HPGe detector was set up at Kalpakkam Reprocessing Plant (KARP) during the year 1998, which is currently being used for routine monitoring of the hull.

Development of neutron based NDA techniques was initiated during the year 1980 and a Neutron Well Coincidence

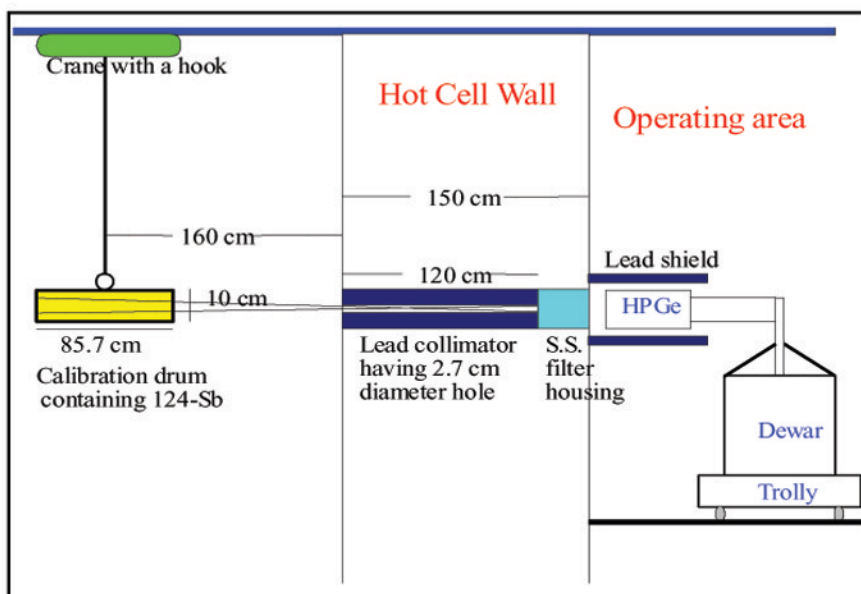


Neutron Well Coincidence Counter

Counter was developed for routine assay of Pu in waste packets and in sealed containers.

Need based neutron coincidence counting systems were developed during the years 1980 to 2003, for the quality control of FBTR fuel pins, pellets, fuel assemblies waste packets and scraps. The developed systems are in routine use. Many innovations in counter design and computer software were also carried out simultaneously to cater to various requirements of the users.

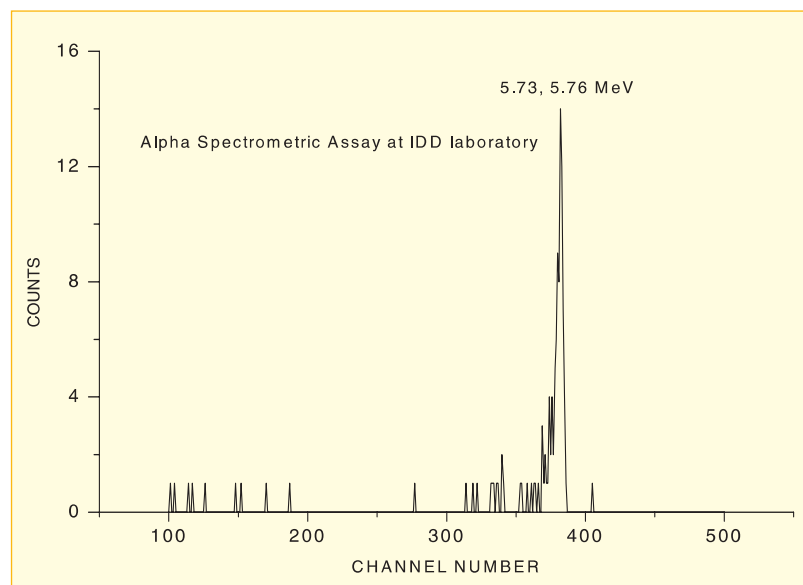
Passive gamma scanners were developed during 1990-2000 for the quality control of FBTR and mixed oxide BWR fuel elements. Uniformity of fissile element distribution, detection of non standard pellets and determination of active length of finished fuel pins are routinely carried out. Efforts are on for the development of integrated gamma and neutron based NDA systems for the second and third stages of the nuclear power programme.



Hull monitor setup at Kalpakkam Reprocessing Plant (KARP)

Synthesis of Isotopically Pure ^{236}Pu Tracer

^{236}Pu is an ideal tracer required for the assay of plutonium in biological and at environmental laboratories of nuclear installations. The $^{237}\text{Np}(p,n)^{236}\text{Pu}$ reaction was used for the synthesis of trace levels of isotopically pure ^{236}Pu by the recoil catcher technique. The surface decontamination of the catcher foils followed by radiochemical separation of plutonium yielded about 200 mBq of tracer grade ^{236}Pu . Electrodeposited Neptunium targets (2.0 mg/cm^2) were irradiated with proton beam ($E_p = 23.5 \text{ MeV}$) at the Pelletron Facility, Mumbai. After irradiation, the stack was cooled for 15 days for allowing complete decay of $^{236\text{m}}\text{Np}$ ($T_{1/2} = 22.5 \text{ h}$) to ^{236}Pu . A method based on solvent extraction was standardised for effective removal of ^{237}Np . About 200 mBq of tracer grade ^{236}Pu activity in 8M HNO_3 was prepared and the activities of $^{238,239,240}\text{Pu}$ as well as ^{237}Np were below the detection limits ($<0.5\text{mBq}$).



Alpha spectrum of plutonium-236

Analytical Spectroscopy of Nuclear Fuels

Spectrochemical analysis of trace impurities in uranium in the early sixties was based on chemical separation of trace elements followed by copper spark atomic emission spectroscopy. In the late sixties, a special campaign was initiated to analyze depleted uranium for determination of rare earths. The trace metal assay of plutonium based fuel samples was initiated in the early seventies. It was based on the ion exchange separation of plutonium from analytes followed by their determination using dc arc emission spectroscopy. Initially the dc

arc - carrier distillation technique was adapted for determination of a large number of trace elements in U/Pu samples without employing chemical separation. Carriers such as silver chloride and gallium oxide have unique ability to sweep impurities from the matrix into the excitation zone without vapourising the matrix thereby avoiding spectral interference. Being refractory, rare earth elements are not vapourised by the carrier. The conventional chemical separation technique is, therefore, valuable for their analysis. A train of three glove boxes was set up which has single bagout port and an entry port. The spectral radiation emanating from dc arc excitation source was transmitted through a quartz window fitted on the sidewall of the train of glove boxes and was collimated on the slit of the spectrograph. The expertise to analyze Pu based fuels was thus demonstrated satisfactorily. In addition to catering to characterisation of Pu bearing fuel materials, the laboratory had also been in the forefront of basic research in the area of analytical spectroscopy of actinides and lanthanides. These activities could contribute to a better understanding of superconducting behaviour of some lanthanide doped materials.

In the eighties a direct reading emission spectrometer with electronic detection system was obtained, which helped in improving the detection limits and precision. Direct reading spectrometer is equipped with two excitation sources viz. dc arc and inductively coupled plasma (ICP). The commercial instrument was adopted for its use for nuclear materials by enclosing the excitation sources in specially fabricated glove-box after the required modifications in the excitation sources.

As part of the R&D efforts, carrier distillation approach was combined with ICP for the direct solid sample insertion into rf heating zone of ICP. Later, the concept was extended to introduction of an electrode of proper shape and size, containing sample solution chemically separated from U/Pu matrix into plasma plume. Another aspect investigated was the improvement of sample introduction into the plasma using graphite furnace with its associated programmable power supply (used in AAS) for vaporization of the analytes from nuclear materials. This method enabled determination of refractory elements such as rare earths in the presence of U/Pu matrix. A high resolution sequential ICP spectrometer adopted for the radioactive work was utilized fruitfully to determine isotopic composition of uranium .



Glove-box adapted direct reading spectrometer equipped with DC arc and ICP excitation sources



Glove-box adopted high resolution ICP Spectrometer

Atomic absorption spectrometry was also utilized to investigate thermodynamics of atom formation and the effects of matrix thereof. The unique approach to determination of impurities in the presence of the refractory matrices was reported for the first time.

Recently, inter-laboratory comparison experiments involving 12 DAE laboratories for analysis of uranium oxide samples was carried out. Based on these experiments five well characterized samples prepared in bulk were certified as DAE reference materials for their use in analytical work. In view of the importance of thorium in nuclear power technology, a similar

campaign is initiated for analysis of ThO_2 and the subsequent preparation of certified reference materials for use in day-to-day analysis of ThO_2 . Analytical support for trace metal characterization of Pu bearing fuel materials has been provided throughout the fuel development programme. The major campaigns successfully executed include development of methodologies for analysis of MOX (Tarapur), U-Al alloy (KAMINI), U_3Si_2 (LEU Fuel), (U-Pu)C (FBTR) and Pu-alloy fuel.

Important Milestones in Analytical Spectroscopy

1. 1975: Development and application of dc arc carrier distillation technique for trace metal characterization of plutonium based fuel samples.
2. 1977: Glove box adaptation of an atomic absorption spectrometer (AAS) unit, with graphite furnace atomizer, for analysis of Pu based samples.
3. 1984: Glove box adaptation of a direct reading spectrometer (DRS) with facilities for both dc arc and inductively coupled plasma atomic emission spectrometry (dc arc-AES and ICP-AES) and its application to analysis of Pu-based samples. Development of Carrier Distillation - ICP approach for analysis of U, Pu.
4. 2000: Development of electrothermal vaporization (ETV) - ICP-AES technique with both radial and axial ICPs.
5. 2001: Organized inter-laboratory comparison experiments (ILCE) involving various analytical laboratories of DAE for trace metal characterization of uranium, leading to adoption of a common analytical methodology and development of five certified reference materials of U_3O_8 for use in DAE laboratories.
6. 2003: Glove box adaptation of a high resolution sequential ICP spectrometer and its application to $^{235}\text{U} / ^{238}\text{U}$ ratio determination.



Glove-box adopted Atomic Absorption Spectrometer with electrothermal atomizer

Actinide Chemistry

In the early sixties, work was initiated on actinides with milligram quantities of Pa, Np, Pu and Am and gram quantities of U and Th. Aim of the work was to provide training to the scientists, metallurgists and chemical engineers in handling of these very hazardous radioactive materials and to carry out basic radiochemical research work as well as developmental work relevant to the reprocessing of irradiated fuel.

Most of the isotopes of these elements are alpha emitters but some of these also emit significant gamma radiations. Work is therefore carried out in glove boxes which are small steel and perspex boxes enclosing miniature laboratories where the chemists work through port holes in the side using long gauntlet gloves to protect themselves and to keep the air box tight. The air pressure in the box is maintained slightly below that of the laboratory in order to ensure that leaks developed inadvertently do not cause contamination of the workers or of laboratory atmosphere.

^{233}Pa tracer was prepared by irradiating ^{232}Th target in APSARA. One of the first interesting Pa chemistry experiment showed that it forms cationic 1:2 complex with $\text{C}_2\text{O}_4^{2-}$ viz. $\text{Pa}(\text{C}_2\text{O}_4)^+$ unlike Np which forms anionic species viz. $\text{NpO}_2(\text{C}_2\text{O}_4)_2^{3-}$. Experiments on Np related to the preferential stabilization of oxidation state 4+ and 5+.

Plan of work on Pu was more elaborate. Conditions for the purification of Pu from fission products and other impurities by anion exchange were arrived at. Kinetics of the redox reac-

tions of Pu was investigated extensively. It was found that conversion of Pu quantitatively to trivalent state in nitric acid/sulfuric acid medium was difficult by reducing agents like iodide, hydrazine or hydroxyl amine. On the other hand cuprous iodide in presence of N_2 was an effective reductant.

Work on the solvent extraction of Pu with the hexone and TBP provided evidence on the nature of Pu(IV) nitrate species in solution and in solvent phase. It was found that the average number of nitrate ions associated with each Pu atom in 1-4 M nitric acid medium is 1.4 and that $\text{Pu}(\text{NO}_3)_4$ is extracted into the organic phase. Work was also initiated on different oxidation states of Pu, disproportionation reaction as well as on radiation chemistry of Pu.

Work on Americium was quite fascinating in view of the gamma activity associated with it. It was possible to follow the path of Am (III) in a chemical reaction using NaI(Tl) detector. On the other hand it was also essential to provide lead shielding while handling large quantities of Am.

Complex chemistry of actinides was investigated in aqueous solution extensively during the sixties. India was one of the few countries who had started contributing to the redox / complexation data in the sixties itself. proton magnetic resonance (PMR), infra-red (IR), ultra-violet (UV) / visible and magnetic susceptibility data was also reported during these years on the solid complexes of U(VI) with a variety of inorganic and organic ligands.

Synergism in actinides

Argonne National Laboratory, USA and Imperial College, London reported an interesting phenomenon in the late fifties in which a mixture of extractants was found to be much better than the sum of the extraction abilities of the two ligands individually. U(VI) was one of the metal ions chosen for these studies. Theonyl Trifluoro Aceton (TTA) was the chelating agent and Trybutyl Phosphate (TBP) was the auxiliary oxodonor ligand. Subsequent work carried out in several laboratories, including BARC, over the next two decades, established that the phenomenon of synergism was widespread and included all the trivalent actinides such as Am(III), Cm(III), Cf(III) and Bk(III), hexavalent actinides such as $\text{UO}_2(\text{VI})$, $\text{PuO}_2(\text{VI})$ and $\text{NpO}_2(\text{VI})$ and tetravalent actinides such as Th(IV), U(IV), Pu(IV) and Np(IV). Prerequisite for the synergism was the large coordina-

tion of metal ion which remains unsaturated with a single extractant (cheating agent). Water molecules invariably enter the coordination sphere resulting in poor organophilicity of the chelate complex. Extensive studies on synergic solvent extraction behaviour of actinide ions resulted in publication of two large comprehensive review articles in structure and bonding and solvent extraction and ion exchange journals. These articles give a summary of this monumental effort.

A variety of phosphorous oxodonor such as tributyl phosphine oxide (TBPO), trioctyl phosphine oxide (TOPO) sulphoxides such as dibutyl sulfoxide (DBSO), diphenylsulphoxide (DPSO), dihexyl sulphoxide (DHSO) and dioctyl sulphoxide (DOSO) amide oxides such as substituted pyridine N oxides were effective synergistic oxodonor which were capable of replacing water molecules in the coordination sphere of metal ions. Beta diketones employed as chelating agents included both linear such as acetylacetonone (ACAC), theonyltrifluoroacetone (TTA), benzoylacetone (BA), dibenzoylmethane (DBM), benzoyl trifluoro acetone (BTFA) and aromatic like pyrazolones and isoxazolones. Extensive synergistic investigations were carried out on hexavalent ions, tetravalent ions and on trivalent ions.

Work on aromatic beta diketones like pyrazolones and isoxazolones was carried out in the late seventies and eighties. Steric and electronic factors were distinctly different for these beta diketones as compared to linear aliphatic beta diketones. Due to non-availability of these ligands commercially, they were synthesized indigenously. As the pKa of these ligands (PMBP and PBI) were distinctly lower than those of linear beta diketones, they were better extractants and were found to be capable of extracting metal ions from relatively stronger acidic media. In the recent years, work has also been carried out to understand complexation behaviour of actinide ions with macrocyclic ligands like crown effects, cryptands and calixarenes. Extraction data on Am(III) with PBI from BARC laboratory was reported in a commemorative volume of 50 years of Transuranium elements. For the first time it was demonstrated that Am(III) could be extracted from 1 M HNO₃ using a synergistic mixture of PBI and TBP. It was also found possible to extract Pu(IV) from 3-4 M HNO₃ using PMBP which could be an alternative to TTA to ascertain the oxidation state of Pu which is a prerequisite for the feed solution in PUREX process.

Actinide Partitioning

It was realized in the early eighties that high level waste devoid of alpha emitters is much safer for disposal to the environment. Raffinate of the PUREX process contains alpha emitting radionuclides such as ²³⁷Np, ²⁴¹Am and ²⁴⁴Cm apart from the residual quantities of U and Pu. In view of the moderate acidity of the high level waste (HLW) (3-4 M HNO₃), TBP is incapable of extracting trivalent Am/Cm and pentavalent Np. The scientists at Argonne National Laboratory, USA designed and synthesized several ligands for extracting selectively trivalent actinides from HLW. Amongst these CMPO (Octyl-phenyl, N N di-isobutyl carbamoyl methyl phosphine oxide) was found to be the most promising reagent which could extract Am(III) and Cm(III) from wide range of acidity (1-6 M HNO₃). In view of non-availability of CMPO commercially, efforts were made for the indigenous synthesis of the extractant. Extensive laboratory data using tracers of actinides and fission products under the conditions prevailing in RR-HLW as well as PHWR-HLW was thus generated. Studies were also carried out on the radiolytic degradation and reusability of the reagent. In 1998, mixer settler studies were carried out on the HAW generated at Fuel Reprocessing Division (FRD), Trombay in a collaborative programme.

Several European countries led by France initiated studies in early nineties on the development of completely incinerable extractants for separation of alpha emitters from high level waste. N N' dimethyl, N N dibutyl tetradecyl malonamide was the most promising of about fifty diamides synthesized and evaluated by a group of radiochemists at CEA, France. A group of separation scientists initiated the work on the evaluation of diamides which were synthesized in collaboration with Bio-Organic Division (BOD), BARC in the year 1997. Few hundred grams of four diamides were synthesized and were evaluated for their extraction behaviour towards Am(III) from varying acidity. Dimethyldibutyltetradecylmalonamide (DMDBDMA) was found to be the most promising and was employed for the generation of extensive laboratory data using tracers of actinides, as well fission products under the conditions prevailing in PHWR-HLW. An attempt was also made to impregnate these extractants on chromatographic supports as well as on polymeric membranes and evaluate their performance for separation of Am(III) from fission products such as ¹³⁷Cs and ⁹⁰Sr.

Alternate Extractants in fuel reprocessing

New challenges of reprocessing high burn up fuels containing large proportions of Pu are proposed to be met by decreasing the contact time of the two phases using centrifugal contactors as well as by redesigning flow sheets with decreased throughputs. In spite of these additional features, efficiency of fuel reprocessing is likely to be compromised. Reprocessing of Th based fuels presents additional challenges like (a) the presence of three recoverable actinides elements, (b) non variable oxidation states of Th (unlike that of Pu) and (c) the presence of U-232 (precursor of hard gamma emitting decay products) in fissile U-233. Innovative approaches in fuel reprocessing were called for to overcome at least some of these problems. In this context R&D work on alternate extractants was undertaken in the eighties with aliphatic sulphoxides (like dihexyl sulphoxide and dioctyl sulphoxide) and in nineties with N,N, dialkyl amides.

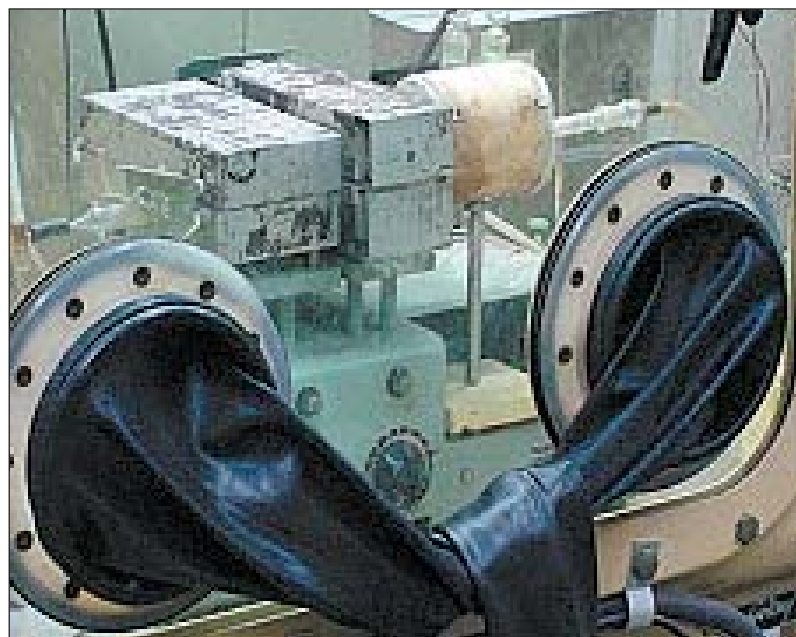
Amides received particular attention as alternate extractants for the reprocessing of spent nuclear fuels in view of (i) the innocuous nature of their degradation products viz. carboxylic acid / amines which can be eliminated easily unlike the degradation product of TBP which require alkali wash and (ii) the possibility to incinerate the used solvent leading to reduced volume of secondary waste and (iii) solubility of dialkylamides in aqueous phase is much lower than that of TBP. In addition, the physico-chemical properties of this class of ligands can be tuned by the judicious choice of the alkyl groups. Mixer settler runs using a mixture of dioctyl butyramide (DOBA) and dioctyl isobutyramide (DoiBA) in aromatic diluents have been reported from CEA, France. Many dialkyl amides were synthesized and evaluated for their physico-chemical properties. Intensive work was carried out on the dialkyl derivatives of hexanamide, octanamide and decanamide in view of the fact that they readily dissolved in n-dodecane and did not form third phase with nitric acid (upto 7 M).

Studies carried at BARC laboratory have shown that: (a) D_{Pu} values are larger for amides than those with TBP at a particular value of U saturation / Pu saturation. (b) D.F. values with respect to F.P's (Zr and lanthanides) are better.

LOC value of Pu (IV) is likely to be larger than that of TBP. These observations therefore indicate particular relevance of dialkyl amides for fast reactor fuel reprocessing, for which about

15 kg of DHOA has been synthesized.

Work on the transport of actinides using membranes im-pregnated with suitable extractants was also carried out extensively in the nineties. In recent years, this work was extended to Polymer Inclusion Membranes and hollow fibre mod-ules. Thermodynamic and kinetic studies were carried out on complexes of interest from analytical as well as environmental speciation. In this context stopped flow spectrophotometry was employed recently to study U(VI)-(BROMOPAD) reaction.



Elemental Analyzer for alpha emitting compounds



Glove Box assembly for Infra-red spectrophotometer

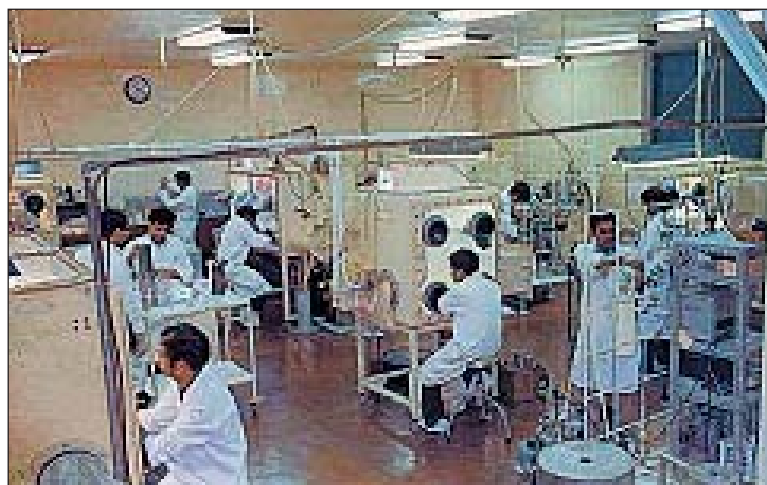
Determination of yield of Pokhran-II Nuclear Tests by Radiochemical Method

India conducted its second series of nuclear tests at Pokhran in May 1998. Though seismic data quickly predict the yield of the device, radiochemical measurements provide more reliable data. The latter require drilling bore holes to extract the core rock samples from the test site. The first hot sample reached Radiochemistry Laboratory at Trombay on 23rd January 1999. The rock sample had turned into glassy phase due to the intense heat generated during the explosion. The gamma-ray spectra of the samples were quite complex and showed typical gamma lines of fission products as well as those of products of neutron induced reactions, viz., ^{22}Na , ^{54}Mn , ^{58}Co , etc. These are formed in reactions having high energy threshold of about 8-12 MeV, e.g. (n,2n), (n,p), etc. These products provided the first evidence of the 14 MeV neutrons generated in the thermonuclear device. These were very exciting moments. The core samples from a large number of bore holes of thermonuclear and pure fission test sites covering a wide range of width and height of the cavity were analysed for the gamma activity and thereby the number of fissions. Integration of the data over the entire volume of the cavity provided the total yield of the devices. Within a time span of six months hundreds of samples were analysed for gamma activity of fission products and other high threshold products. Radiochemical analysis provided trustworthy data for the tests thereby ending any controversy over the yield values. Later, *in-situ* gamma logging of the bore holes was also carried out using a CdZnTe detector.

FUEL CHEMISTRY PROGRAMME

Chemical Quality Assurance for the Nuclear Fuel Cycle Determination of half-lives of actinide nuclides

Half-lives of a number of actinide nuclides are determined employing mass spectrometric and alpha spectrometric methods. Large variation in the half-life values (13-15 years), for example, of Pu-241, necessitated a re-look into its value. It has been determined by parent decay method, and daughter growth method. In the parent decay method, change in isotope ratios $^{241}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{240}\text{Pu}$, and $^{241}\text{Pu}/^{242}\text{Pu}$ was studied periodically by a thermal ionization mass spectrometer. In the daughter growth method, the half-life was obtained in four independent ways. These were (1) alpha spectrometry taking ^{239}Pu and ^{242}Pu separately as reference isotopes and studying periodically the increase in alpha activity ratio, (2) alpha proportional counting for observing periodically the change in total alpha activity, (3) isotope dilution alpha spectrometry (IDAS) using ^{243}Am as a spike, and (4) isotope dilution mass spectrometry using ^{243}Am as a spike. A half-life value of 14.4 years was recommended for Pu-241. Similar concerted efforts resulted in accurate half-lives of ^{232}U , ^{233}U , ^{238}Pu , ^{240}Pu , ^{242}Pu , ^{241}Am , ^{243}Am , ^{242}Cm , and ^{244}Cm nuclides. It should be mentioned that based on this work IAEA recommended revision of half-lives of ^{232}U and ^{241}Pu nuclides. Further, long-standing discrepancy of more than 6% in half-life of ^{242}Pu determined by different methods could be resolved by adapting a more rational and rigorous approach using mass spectrometry.



An inside view of the laboratory

Fission yields of stable fission products by mass spectrometry

Thermal ionization mass spectrometry was employed to determine fission yields of stable fission products in thermal neutron induced fission of ^{235}U , ^{239}Pu and ^{241}Pu nuclides. This helped in augmenting the fission yield data on stable fission products and supplementing data available from radiochemical measurements on unstable fission products. The data obtained on rare earth fission products were quite significant in the sense that these are stable nuclides and are formed in not so significant amounts and thus require sophisticated and sensitive instrumentation techniques for their determination. Mass spectrometric procedures were also standardized for direct determination of fission product nuclides without resorting to any separation from the corresponding actinide nuclide. This had eliminated uncertainties in the recovery of fission products during separation enhancing reliability in measurements.

Recently, procedures were also established for analysis of fission gases Kr and Xe from test fuel pins of MOX fuel as a part of post-irradiation examination of irradiated fuels employing quadrupole mass spectrometry (QMS). The isotopic ratios of $^{131}\text{Xe}/^{134}\text{Xe}$ and $^{132}\text{Xe}/^{134}\text{Xe}$; $^{83}\text{Kr}/^{86}\text{Kr}$ and $^{84}\text{Kr}/^{86}\text{Kr}$ were measured. From these isotopic ratios as well as from Xe/Kr ratio, it was possible to establish that majority of fissions are from ^{239}Pu . The fission product ^{85}Kr is radioactive and subsequently decays to ^{85}Rb . From the measured $^{85}\text{Kr}/^{86}\text{Kr}$ ratio and from the expected total fission yield of mass number 85, a cooling time of about 12 years was estimated, which was very near to the actual value.

Actinide and Process Chemistry

The search is still on to develop new reagent combinations and devising new separation procedures for actinides. This area of research in chemistry of actinides broadly aims at (a) basic understanding of complexation behaviour and (b) devising improved separation schemes relevant to reprocessing and waste management. Chemical and radiochemical investigations on actinides from Ac to Cf were carried out in all their available oxidation states. The basic research programme on actinide chemistry included investigations on the interconversion of oxidation states of actinides with a view to arrive at suitable

conditions for preferential stabilization of each of the oxidation states; studies on the complex forming abilities of actinides with different inorganic and organic anions; studies on the solvent extraction behaviour of actinide ions into different types of solvents from varying aqueous environments; studies related to both cation and anion exchange behaviour of actinides etc. The understanding of their chemistry forms the backbone in developing methods for their estimation as well as their recovery and purification from different complex matrices.

Recovery of Pu from various types of waste solutions was effected by precipitating Pu as Pu (III)-oxalate followed by thermal decomposition of the oxalate to obtain PuO_2 . A method was developed for recovery of Pu from the oxalate supernatant by precipitating Pu as ammonium plutonium (III)-oxalate on addition of 0.5 M $(\text{NH}_4)_2\text{SO}_4$ or NH_4Cl . The supernatant obtained contained Pu within disposable limits. The ammonium plutonium (III)-oxalate decomposed at 400°C yielding pure PuO_2 .

A method was standardized for recovery of plutonium from phosphate analytical waste solutions (about 400 mg Pu/L). The analytical waste also contained Fe(III), which was utilized for co-precipitation of phosphates of ferric along with phosphates of plutonium at a pH around 3 by careful addition of NaOH.

During the analysis of U-Zr-Al samples for their uranium content, phosphate waste containing significant amount of U was generated. This waste was processed for recovery of uranium by co-precipitating uranium with the Fe (III) hydrogen phosphate. The precipitate obtained was dissolved in concentrated hydrochloric acid so as to recover uranium from it by ion-exchange technique. The liquid waste accumulated during the leaching of active glove-box gloves containing Pu and Am and other acid waste solutions were processed to remove Pu and Am.

Anion exchange studies on plutonium recovery with a large number of gel type and macroporous resins conducted in our laboratory have widened the scope of plutonium recovery from different sources yielding a pure and concentrated plutonium product.

Several solvent extraction/ion exchange/extraction chromatographic procedures were developed during the eighties and nineties, which improved recovery of the Pu from different types of analytical waste streams. Elegant methods were

proposed for determination of Pu (IV) in feed solution of PUREX process (using a pyrazolone) and for determination of ^{90}Sr in waste solution (using substituted crown ether).

Studies on the solution chemistry of actinides resulted in introducing innovations to improve the process performance as well as in the recovery of many byproducts of fuel reprocessing. Initial parameters for the fuel reprocessing plant at Trombay were optimized.

Earlier investigations on the preparation and performance of tetravalent uranium as an alternative partitioning agent between uranium and plutonium, in place of ferrous sulphamate, led to successful introduction of this reagent in the Power Reactor Fuel Reprocessing (PREFRE) plant at Tarapur and at the Kalpakkam Reprocessing plant. Detailed investigations were carried out for recovery of neptunium as a byproduct of PUREX process. Large data generated on neptunium behaviour in PUREX process has found a place in the standard text book on nuclear chemical engineering by Benedict and Pigford. The extensive studies on the complex formation behaviour of neptunium carried out at BARC are also well recognized in scientific literature on neptunium complexes.

Studies on irradiation of ^{237}Np targets and their processing for recovery of ^{238}Pu enabled establishing methods for the preparation of ^{238}Pu sources, which have many applications as an isotopic power generator. Large scale plutonium recycling operations carried out for meeting the Pu required for FBTR fuel enabled developing methods for recovery of gram quantities of americium which has many applications in gamma radiography as well as in smoke detectors. This americium could be used in measuring the uranium concentration profile in reprocessing plant streams with on-line detection.

Though TBP is employed universally for reprocessing irradiated nuclear fuels in the well known PUREX process, there are a few limitations for its use with high burn up fuels with high Pu content and high radiation field. N, N-dialkyl aliphatic amides hold promise as alternate extractants to TBP in view of their complete incinerability and benign nature of their degradation products. Extensive work carried out on di-n-hexyl octanamide revealed that it extracts Pu (IV) more efficiently than TBP. It was also observed that decontamination factors (DF) values for U and Pu from Zr are favourable for amides as compared to TBP. Mixer settler studies suggest the possibility of quantita-

tive stripping of uranium in less number of stages as compared to TBP. In view of their poor Th (IV) extraction, branched trialkyl phosphates and dialkyl amides were found to be promising for the separation of ^{233}U from irradiated Th as alternative to TBP in THOREX process.

Distribution studies of Am employing another versatile extractant viz. Try alkyl phosphene oxide (TRPO) (Cyanex-923), were initiated after prior separation of U.

Thermodynamic data on Th (IV) / Ln (III) with ligands of environmental interest was obtained and correlated with fundamental properties. Stability constants of fluoride complexes of Ce (III) and La (III) determined by ion selective potentiometry were in agreement with estimated values obtained by interpolation from the general trend of stability constants of lanthanide fluorides in aqueous solution. Correlation of stability constants of fluoride complexes of lanthanides with their fundamental properties like ionic charge, coordination number, ionic radius and electronic configuration was studied. Stability constants of thorium hydroquinone complexes are not available in the literature, therefore the work was undertaken to study these constants. Attempts to study the hydrolysis behaviour of Th (IV) in presence of quinhydrone indicated the complexation of hydroquinone (HQ) with thorium. The analysis of titration data appears to indicate formation of only one species $\text{ThQ}_n(\text{OH})_4$.

Chemical Quality Control of Nuclear Materials Mass Spectrometry

Isotopic mass of an element determines its nuclear properties including fission and absorption cross sections. Measurement of isotopic composition of materials used in nuclear technology is, therefore, very important. The most precise measurements are made by mass spectrometry. R&D activities in this field were initiated in 1970 with the availability of CH-5 magnetic sector Thermal Ionisation Mass Spectrometer (TIMS). This instrument was extensively used until 1980 for developing analytical methodologies for determination of isotopic composition and concentration of different elements from Li to Cm. Detailed theoretical computations were also carried out to elucidate the requirement of choice of the molecular ion ratios for error-free mass spectrometric measurements in the case of Li and B. It should also be mentioned that the mass spectrometric analysis of boron by monitoring Cs_2BO_2^+ ion was the first

ever in the world. In addition to measuring isotopic composition, mass spectrometric technique can also be used for Isotope Dilution Mass Spectrometry (IDMS) using suitable spikes e.g., ^{233}U .

In the mid 70's, Radiochemistry Division of BARC participated in three inter-comparison experiments (IDA-72, PAFEX-I and PAFEX-II) organised by international agencies to evaluate precision and accuracy achievable on measurements of U and Pu, and BARC results were among the best.

Development of tracer techniques for the determination of plutonium at a reprocessing plant site was another significant and unique contribution employing mass spectrometry. Plutonium, which is produced in a nuclear reactor as a result of neutron irradiation of ^{238}U isotope is another important fissile nuclide and also has strategic importance. Reprocessing plant is the first stage at which plutonium enters the nuclear fuel cycle and its accurate determination is of paramount requirement. The irradiated fuel is dissolved and the "dissolver solution" is fed into an input accountability tank. Conventionally the tank volume and density of solution are needed to estimate plutonium. The tracer techniques eliminated these requirements. It is based on simple mathematical relation of ratio-proportion. A known amount of tracer element (either Mg or Pb) is thoroughly mixed in the dissolver solution present in the accountability tank. A small aliquot is taken and the ratio of Pu to tracer is determined. Knowing the initial amount of tracer element added, it is possible to accurately calculate total amount of Pu present in the tank. BARC has been first to demonstrate the feasibility of this technique on the plant scale.

The concentration of a given element is determined by thermal ionization mass spectrometry employing isotope dilution technique. Known concentration of the same element with different isotopic composition from that present in the sample is added. This added element is called "spike". After thorough mixing an aliquot of the mixture is analyzed for measuring the change in the isotopic composition. From this, it is possible to calculate the concentration of the element present in the sample. Plutonium is no exception and ^{242}Pu spike was being used in the isotope dilution technique for Pu determination. This ^{242}Pu spike is not commercially available to India and there are many international restrictions. Efforts were made, therefore, to develop alternate spikes/techniques to circumvent this problem.



Mass spectrometer setup at Radiological Laboratory BARC, Trombay

The research and development efforts culminated in the development of an entirely independent method based on alpha spectrometry. This method is christened as isotope dilution alpha spectrometry (IDAS). The principle of IDAS is similar to that of isotope dilution. In IDAS, indigenously produced ^{238}Pu spike is added to Pu solution and instead of measuring the change in isotope ratios by thermal ionization mass spectrometry, the change in alpha activity ratios of Pu isotopes is measured by alpha spectrometry. The development of IDAS has been one of the most significant contributions towards our efforts at achieving self-reliance in nuclear technology.

With the advent of high-sensitive and multi-collection detector systems, it was possible to demonstrate that isotopic fractionation is the limiting factor responsible for uncertainty in isotopic measurements. By optimizing experimental conditions such as reproducibility in sample loading, sample size, rate of heating, temperature of heating and data collection time, it was possible to realize limiting uncertainties of better than 0.01% in isotopic ratio measurements. This expertise in accurate mass spectrometric measurements was also fruitfully exploited in identifying suitable alternative spike isotopes for Pu determination. Thus, in addition to not easily accessible ^{242}Pu spike, BARC demonstrated that Pu from power reactors can be used as spike to determine Pu from research reactors and vice-versa. That's because Pu from these reactors has different isotopic compositions and on mixing there would be significant change in isotopic ratios.

For an interference-free isotopic analysis of rare earth elements it is essential that the adjacent rare earths be separated from one another to eliminate isobaric interferences. This is an important and necessary requirement for determination of burn-up of irradiated nuclear fuel. Conventionally, ion exchange separation procedures involving three stages were used. In the first stage, U and Pu are separated from fission products. In the second stage, rare earth elements as a group, are separated from other fission products. In the last stage, Nd is separated from other rare earth elements. Extensive experiments were carried out to understand the absorption behaviour of rare earth elements on anion exchange resins from mixed-solvent (methanol-water) media. Based on these, a two-stage ion exchange separation procedure was standardized for purifying Nd from the rest of the fission products including other rare earth elements, particularly Ce and Sm. The new procedure not only reduced the time of separation but also helped in improving accuracy in burn-up measurements.

This scheme of Nd separation could be fruitfully employed in the field of geochronology also. Sub-ppm levels of Nd and Sm were separated from granite rocks from Singbhum region and the first dating measurements using $^{147}\text{Sm}/^{143}\text{Nd}$ dating pair were reported from this country.

Alpha spectrometry is another important area where BARC had significant contributions. In this technique, alpha emitting radioactive nuclides such as majority of actinides can be monitored by measuring alpha activity emitted by them. The energy of the emitted alpha particle is a unique signature of the nuclide. Thus, an alpha spectrum is obtained if there is more than one alpha energy. But unfortunately the energy of alpha particles get degraded even as they are being detected. This results in a diffused and overlapped alpha spectrum, where the lower end of the energy spectrum has contributions from the high energy end of the spectrum, thereby rendering the measurements inaccurate. Again, by carefully selecting experimental conditions for preparing the alpha source and also developing a mathematical expression for evaluating the alpha spectrum to account for the high-energy contribution at the low energy end, BARC demonstrated its acumen in meeting the unexpected challenges. The method of geometric progression used to adequately explain the shape of the alpha spectrum is unique in the sense that an accurate alpha activity ratio can be obtained.

Small is beautiful

Hydrogen is the lightest of all the elements but its effect on the performance of the zircaloy coolant channels of pressurized heavy water reactors (PHWRs) is “heavy weight”. Zircaloy channels, over a period of continuous usage in reactors can become brittle due to formation of hydride/deuteride thus severely limiting the life of these channels. The ageing management of zircaloy channels therefore needs to be addressed from the point of view of hydrogen/deuterium determination. India has a number of PHWRs and an accurate method for hydrogen determination in zircaloy needed to be established. Two significant research contributions were made in this direction. Both made use of mass spectrometry. In the first method, a two-level exposure technique was developed to determine hydrogen in zircaloy employing spark source mass spectrometry (SSMS). Until this method was established, SSMS, though a multi elemental analysis technique was reported to be not amenable for hydrogen determination because of its “pre-dispersion” in the mass analyzer itself. For the first time, using the two-level exposure technique, it was demonstrated that even hydrogen could be determined employing SSMS also.

The second method is based on hot vacuum extraction-quadrupole mass spectrometry (HVE-QMS). Necessary vacuum extraction system was indigenously fabricated to suit the unique requirements of hydrogen determination. As little as 10 mg of zircaloy sliver samples are adequate for determining both concentration and isotopic ratios of hydrogen. Hundreds of sliver samples received from different PHWRs in the country were analysed by this technique. The isotopic data was quite useful not only in validating the theoretical computational codes but also in assessing the annual deuterium pick-up rate. This exercise demonstrated the symbiosis between research and its immediate direct application.

Analytical Methodologies developed

Chemical quality control of plutonium bearing fuel materials is an important facet of the nuclear fuel cycle. A number of innovative methods were developed for the purpose. For simultaneous determination of ultra trace amounts of boron, fluorine and chlorine in different nuclear fuel systems a new method employing ion chromatography after their separation by pyrohydrolysis was developed. Erratic results obtained

sometimes for fluorine concentration, particularly in carbide samples, were found to be due to interference from acetate ion, which could also be produced during pyrohydrolysis. Extensive experimental optimization of parameters resulted in eliminating this small but significant interference.

Another important application of ion chromatography was in the environmental studies. The cyanide contamination at sub-ppm levels in potable water was investigated and an IC method was standardized for the determination of cyanide. Experiments revealed that the decay of cyanide followed the first order kinetics, which also depended on the presence of chloride ions in water.

An NDA Gamma assay method for simultaneous determination of Pu and Am in solid scrap using NaI(Tl) detector and a multichannel analyser for Pu in the range of 50-80 mg and Am in the range of 0.2-1.0 mg per kg of sample was developed and is being used for their assay of wastes generated during plutonium fuel fabrication.



Segmented gamma scanning assembly for 200L waste drum to screen solid alpha waste

For determination of sulphur, a method based on vacuum combustion extraction, quadrupole mass spectrometry was developed. The technique involves combustion of the sample in the presence of oxygen supplier like UO_3 under static vacuum conditions, extraction of the gases released into a known volume, measurement of pressure and determination of the

composition of the gas by on-line quadrupole mass spectrometer. The sulphur content is then calculated employing gas laws.

Studies on sulphur speciation employing ion chromatography were carried out with different mobile phase concentrations to reduce the retention time of thiosulphate without compromising resolution between sulphite and sulphate peaks. Experiments were carried out with industrial effluents and water samples received from different locations. The sulphide content in these samples was determined by iodimetric titration for comparing with ion chromatographic values.

An XRF method was standardised for determination of Th in total (U + Th) in sintered UO_2 - ThO_2 , having UO_2 % from 1-3% in powder samples. Another method based on the same principle was developed for determination of Ga and U present in the mixture of their solid oxides.

For separation and determination of lanthanides by chelation ion chromatography technique, experiments were carried out for exploring the feasibility of analysing lanthanides in different nuclear materials and a quantitative differential pulse voltammetry method for determination of nanogramme of Cd in ThO_2 matrix without any chemical separation, was established.

Inter Laboratory Comparison Experiments (ILCE), for the certification of U_3O_8 material doped with known concentration of trace elements were carried out using inductively coupled plasma mass spectrometry (ICP-MS). For quantification of results, La was used as internal standard for rare earths elements and for general elements; a CRM sample was taken as the external calibration standard. The ICP-MS instrument was also used to establish analytical methodology to determine Gd content in (U,Gd) O_2 samples without resorting to any chemical separation procedures, which is a prior requirement for other techniques.

ICP-MS technique was also successfully employed to determine boron isotopic ratios in a number of refractory matrices. The advantages include reduced time of analysis, reasonable precision and accuracy and large sample throughput.

A method based on combustion-cum gas chromatographic technique was established for determination of free and combined carbon in uranium metal. To remove residual carbon from starting materials prior to the fuel fabrication steps, one has to know whether carbon is present in free (graphite) or combined (UC) form. A method was developed wherein the

sample is subjected to combustion at different temperatures.

The feasibility of a biamprometric method was evaluated for determination of uranium in the microgram range (5 ÷ g to 300 ÷ g) by direct titration as well as by standard addition method. The method is found to be satisfactory with a precision of 0.2% at 300 ÷ g, 1% at 50 ÷ g and 5% at 10 ÷ g levels.

Isotopically pure ^{232}U is required for direct use in spectroscopic investigations involving LASERS. Preferred method of producing isotopically pure ^{232}U is through irradiating ^{231}Pa . About 290 microgram of ^{232}U has been recovered from irradiated Pa containing Zr, Ti, Nb and Si impurities first by using solvent extraction with 30% Tributyl Phosphate (TBP) in Carbon tetra chloride solvent and trace amount left after extraction was further recovered by precipitation in alkaline media with hydrogen peroxide. The recovered U was further purified using solvent extraction with 0.5M Thenoyl Trifluoroactone (TTA) in carbon tetra chloride. This was the first time that this methodology was demonstrated in BARC.

Rubidium uranium sulphate and potassium plutonium sulphate have been synthesized and demonstrated to have all the qualities of chemical assay standard materials.

X-ray and Solid State Chemistry

Earlier investigations centered around understanding complex actinide oxide systems and plutonium carbides using X-ray Diffraction and thermal techniques. The structure of PuTe_2O_6 was derived by Rietveld analysis of X-ray powder diffraction data. The structure is made of zigzag strings of PuO 's distorted edge-sharing polyhedron parallel to α -axis in the monoclinic unit cell. Each plutonium atom is coordinated to eight oxygen atoms and each tellurium atom is coordinated to three oxygen atoms. The kinetics of decomposition of PuTe_2O_6 was studied by isothermal methods to obtain the rate constant, activation energy and reaction mechanism. The structure of $\text{K}_8\text{Ca}_2\text{U}_6\text{O}_{24}$, $\text{K}_8\text{Sr}_2\text{U}_6\text{O}_{24}$ and $\text{K}_8\text{Ba}_2\text{U}_6\text{O}_{24}$ were derived from X-ray powder diffraction data, and structural parameters were refined by the Rietveld profile method. The structure consists of uranyl octahedra and regular octahedra of oxygen atoms around Ca, Sr and Ba atoms.

X-ray, thermal, IR and NMR studies have been carried out on a number of uranium and plutonium compounds for structure elucidation. The single crystal X-ray structure of the com-

plex $[\text{UO}_2(\text{TTA})_2 \cdot \text{H}_2\text{O}]$ crown ether shows that two of the $[\text{UO}_2(\text{TTA})_2 \cdot \text{H}_2\text{O}]$ molecules are bridged by the crown ether ligand to give a dinuclear complex $[\text{UO}_2(\text{TTA})_2 \cdot \text{H}_2\text{O}]_2$ (Crown ether). Two such dinuclear complexes are stabilized by the intermolecular hydrogen bonding to give a stable tetra nuclear cluster.

It has been established that up to 30 mole % PuO_2 (Pu^{4+}) can go in to solid solution in the stabilized zirconia, a fluorite matrix in air at 1400°C . It was of interest to see the solid solubility of Pu^{3+} , the sample of stabilized zirconia containing 20 mole % of plutonium oxide was mixed with calculated amount of graphite (to reduce Pu^{4+} to Pu^{3+}) and heated in helium atmosphere up to 1400°C . A loss in weight was observed from the thermogram above 1000°C , due to reduction of Pu (IV) to Pu(III). The X-ray powder diffraction pattern of the reduced product was found to be a single fluorite phase with a small increase in lattice parameter, indicating Pu(III) can go into solid solution in the stabilized zirconia.

The crystal structure of $\text{Pu}_2\text{Zr}_2\text{O}_7$ was derived from the analysis of X-ray powder diffraction data by Rietveld analysis. The systematic absences in X-ray reflections required by the pyrochlore structure [Fd3m] were observed in the indexed pattern with cubic cell parameter of $a = 10.5719$ (1) Å and $Z = 8$. In the structure, each Zr cation has 6 oxygen anions in octahedral coordination.

High Temperature Thermodynamics

Development of chlorination volatility process for thorium based fuels was an active programme in the sixties. After winding down the Molten Salt Breeder Reactor (MSBR) programme, it was decided to study the volatility behaviour of U-Th halides for subsequent application in non-aqueous processes. A number of facilities for measurements of vapour pressure using transpiration, Knudsen effusion, boiling point and isopiestic methods were set up. The vapour pressure techniques were also used to study thermodynamic properties of Bi-A1loys relevant to MSBR programme. The technique base was expanded by including solid oxide electrolyte galvanic cells, isoperibol solution calorimeter and high temperature Calvet calorimeter .

Solid oxide electrolyte galvanic cells, Knudsen effusion mass loss and Knudsen effusion cell mass-spectrometric

methods were used to determine vaporisation behaviour of UC, (U,Ce)C, UN, stainless steel, Pd, Rh, Tellurides of U and Th and molybdates of alkali metals. The noteworthy feature of all the above investigations was that all the thermodynamic properties of a system were determined by the same laboratory using a variety of techniques.

For the FBTR at Kalpakkam, a fuel, which could provide high fissile content without the use of enriched uranium, was required. $(U_{0.30}Pu_{0.70})C$ with 5-15% sesqui carbide content and very small amounts (< 1000 ppm) of O_2 and N_2 was required. However, it was observed during the fabrication that it was not possible to achieve low N_2+O_2 content without significant loss of Pu by volatilisation. With proper optimisation of parameters, a fuel having 5000-6000 ppm of oxygen and 500 ppm of nitrogen could be obtained. The compatibility of the fuel with S.S cladding could not be easily established on the basis of available literature. An experimental programme was launched with participation of a large number of scientists from Fuel Chemistry Division, Radio Metallurgy Division and Metallurgy Division of BARC. The results of these investigations established chemical compatibility of the fuel fabricated with SS cladding. It is heartening to note that this was borne out by actual experiment on the FBTR fuel, which has reached a burn up of 140,000 MWD/T.

For the second core of FBTR, there was a proposal at one time to use mixed nitride fuel. Theoretical calculations established that good chemical compatibility can only be achieved if the fuel has very low carbon content and a separate mixed oxide phase.

$(U, Th)O_2$ is a nuclear fuel proposed to be used in the advanced heavy water reactors. Hence, it is necessary to investigate thermophysical properties of this fuel in the reactor operating conditions. In this context, the C_p values of this alloy were determined employing differential scanning calorimetry (DSC) with a predefined heating programme. The C_p values were determined for the mixed oxide containing 0%, 2%, 4%, 6%, 10% and 20% uranium. The experimental values were similar to those of thorium oxide (ThO_2). Heat capacity measurements were also made on uranium + 6 w % molybdenum over a temperature range of 373 to 573 K, on U-Zr system in the range 373 to 923 K and on $U(Al, Si)_3$ in the temperature range 323 to 823 K to study their thermophysical properties.



High temperature studies in the glove box

Heat capacities $Rb_2U_4O_{11}(S)$ and $Tl_2U_4O_{11}(S)$ were obtained using a high temperature calorimeter from the enthalpy increment data in the temperature range 310 to 1000 K. Thermochemistry of interoxide compounds in the system M-Te-O where M is a fission product, is of considerable interest to understand the chemistry of the oxide fuel pins in an operating nuclear reactor. The Gibbs energy of formation of $Ba_3Te_2O_9(S)$ was determined using transpiration technique in the temperature range 1119 K to 1280 K. Gibbs energy of formation of $CaRuO_3(S)$ has been obtained using solid electrolyte galvanic cells employing both oxide and fluoride conductors (calcia stabilized zirconia, calcium fluoride) in the temperature range 814 to 1235 K.

Studies on Fuel Materials

Research on fuel materials at BARC started during sixties with the preparation of plutonium oxide. Very soon it was decided to study the plutonium metal preparation and assemblies were set up for hydrofluorination to convert plutonium fluoride to plutonium metal. At one gram level, it was very difficult to get the consolidated metal, particularly as no dry glove box assemblies were available. The programme on the Pu metallurgy gradually evolved to the development of non-aqueous method in which a variety of molten salt equilibria were investigated. In 1969, the Molten Salt Breeder Reactor being developed by Oak Ridge National laboratory (ORNL), USA appeared most promising reactor for thorium utilisation and an elaborate chemical research programme was chalked out. MSBR work

carried out studies on the solubility behaviour of PuF_3 and established adequate solubility in a large number of salt compositions having LiF , BeF_2 and ThF_4 . Molten salt liquid metal equilibria for on-line reprocessing of MSBR fuel was also initiated at that time. With the winding down of MSBR programme in USA, the emphasis on this programme was reduced in BARC also.

In the seventies there was a requirement of Pu metal for making a nuclear explosive device and the experiments in the Radiochemistry Division of BARC, were used for preparing PuF_4 required for this programme. The work of the high temperature group was divided into two parts. One dealing with the preparation of fuel material preparing sol-gel process and the other dealing with high temperature thermodynamic systems relevant to Indian programme.

Sol-Gel Technology for Fuel Development Programme

This programme was taken up with a view to developing a fuel fabrication process suitable for remote handling of Pu and ^{233}U based fuel materials. Conventional powder-pellet fuel fabrication processes are not well suited for such handling inside the shielded facilities as they involve a large number of mechanical steps.

Studies on the preparation of ThO_2 and $(\text{U,Th})\text{O}_2$ microspheres using the sol- dehydration process were initiated. The required equipment was successfully fabricated and installed in a fume-hood. A precipitation peptisation process for the preparation of 3 M sols of ThO_2 , and $(\text{Th,U})\text{O}_2$ was developed. Several batches of ThO_2 and $(\text{Th,U})\text{O}_2$ microspheres were prepared and sintered to ~95% theoretical density (TD) microspheres. Several batches of 500 g UO_2 microspheres of 700 mm diameter with > 98% TD were prepared. A gelation assembly was setup in a series of three glove- boxes to prepare $(\text{U,Pu})\text{O}_2$ microspheres containing 5 to 15% plutonium.

With induction of special facilities like walk-in fume-hoods and tall glove-boxes studies on the development of chemical conditions for internal gelatin process (IGP) culminated in the formation of gelation field diagram for prediction of gelation behaviour of uranium nitrate solution could be carried out. Similar studies were conducted for the preparation of defect free ThO_2 and $(\text{Th,U})\text{O}_2$ microspheres of desired size and composition.

A new gelation equipment was developed with a fully auto-

mated gelation column and the horizontal vibratory feed nozzle. It increased the production rate for 2.1 mm dia gel microspheres to 1.2 kg/ UO_2 micro spheres per hour per nozzle. The new gelation equipment was housed in a wa1k-in fume-hood. A 10 kg/batch oven was also commissioned for drying of the washed gel particles.

A programme was undertaken to develop Sol-Gel Microsphere Pelletisation (SGMP) process for preparation of UO_2 pellets of PHWR specifications. In this process, carbon containing UO_3 gel particles from which carbon was removed during controlled calcination process and the resultant porous microspheres were reduced and pressed into UO_2 pellets, which were then sintered. About 250 kg of such gel particles were supplied. These were converted to UO_2 pellets and loaded in PHWR fuel bundles. Two such bundles were successfully irradiated at MAPS II up to 10,000 MWD/T burn up.

The carbon containing gel panicles of urania were used to study carbothermic reduction of UO_3 to UC microspheres. The process parameters were also optimized for preparation of (U,Ce) C, UN, and (U, Ce) N.

The process of UO_2 preparation was further improved by optimisation of carbon free route and Low Temperature Sintering (SGMP-LTS) furnace. The result with the first few lots of the pellets have shown remarkable improvement in the quality and the throughput of the pellets.

During the VIII plan period a sol-gel facility was planned at the Advanced Fuel Fabrication Facility, Tarapur and is presently under installation. The facility when commissioned, will have a capacity to produce about 10 T/y $(\text{U,Pu})\text{O}_2$ microspheres of different compositions.

Work was carried out to study the vibro-compaction of microspheres for the preparation of sphere-pack fuel pins for the fast reactor applications. Future programmes include the development of coated panicle fuels for high temperature gas cooled reactors, SGMP process for the Th- ^{233}U based fuels, irradiation behaviour studies of the vibro-compacted fuel pins etc.

Sol-Gel Technology for Non-Nuclear Materials

Another important achievement was exploitation of this sol-gel technology in non-nuclear applications viz. for development of high surface area catalysts in petroleum industry, high

of high surface area catalysts in petroleum industry, high purity Nd_2O_3 for laser applications etc. Studies were carried out on the preparation of porous titania microspheres by internal gelation technique by adding cationic surfactants such as Cetrinide ($\text{C}_{17}\text{H}_{38}\text{BrN}$) or CTAB ($\text{C}_{19}\text{H}_{42}\text{BrN}$) in the feed broth prior to gelation. Batch experiments on the sorption of tetravalent ions particularly Pu(IV) on this material from various carbonate/bicarbonate solutions showed high distribution ratio values in the range of 600 to 1500 indicating suitability of this material for removal of plutonium from carbonate waste streams. Disc electrodes made of haematite doped with Mg, Si, Ti, Zr and Ca were prepared by sol-gel methods to investigate their use in photo-electrochemical cells. With the aim of technology development for phosphors based on rare-earth doped materials, YAG (Yttrium Aluminium Garnet) doped with Ce^{3+} was synthesized by Gel Entrapment Technique and the samples were characterised by different techniques.

Sol-gel technique was used to prepare pellets of $\text{Bi}_2\text{O}_3\text{-BeO}$ to be used for rechargeable neutron source. Homogeneous mixture of Bi_2O_3 and BeO in the form of cylindrical pellet were irradiated to give neutron yield of 5000 n/sec/cc. A novel type of low-cost Po-Be source, which is rechargeable, was developed. The device is a convenient short-life source having negligible gamma dose and can be recharged in a reactor whenever the neutron yield falls below a specified strength.

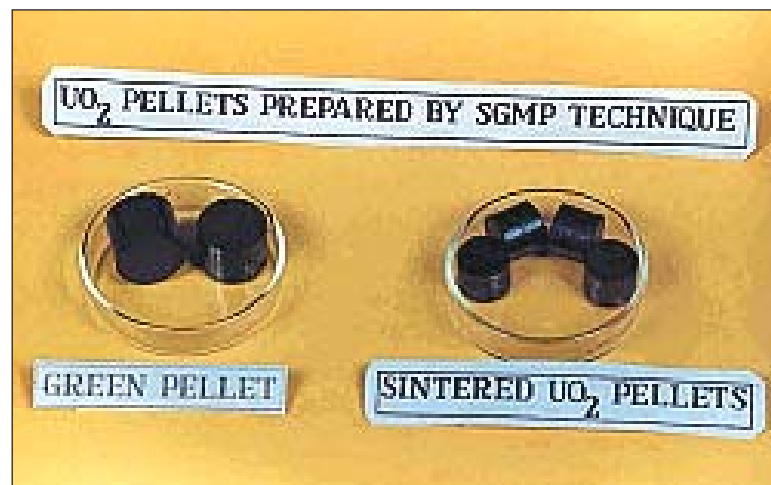
Large size crystals of neodymium-doped YAG are used as lasing medium and are presently imported at high cost. With a view to preparing such crystals indigenously, kilogram scale batches of high purity Nd-YAG powder were prepared by gel entrapment technique, maintaining dust-free conditions. The quality of the powder was ascertained by XRD, surface area analysis, scanning electro-microscopy (SEM) and spectrographic analysis.

High surface area alumina microspheres of controlled porosity are of immense use as a base for a variety of catalysts and for several other applications. Internal gelation technique was exploited to prepare good quality alumina gel spheres.

Analytical Services

To ensure stringent specifications, chemical quality assurance of nuclear fuel requires accurate analysis of various

major and minor metallic and non-metallic constituents present in it. Analysis of the samples were carried for the following specifications: U, Pu and Th by Electrometric and Complexometric techniques. Isotopic abundance measurements of B, U, Pu etc. by Mass Spectrometry. ^{241}Am content in Pu samples by Alpha spectrometry. Gaseous analysis



by Gas chromatography and Quadrupole Mass Spectrometry. Phase identification by X-ray diffraction. Trace non-metallics by pyrohydrolysis followed by Ion Chromatography. C, H, N, O determinations by various Element Analysers. Hydrogen and deuterium in coolant channels by Hot vacuum technique with an on-line Quadrupole Mass Spectrometry, Surface area and porosity measurements by BET method. Moisture in fuel samples. Oxygen/metal (O/M) determination in oxide samples and Material characterisation by thermal and spectroscopic techniques.

Human Resource Development

Chemical research in all areas related to nuclear science and technology helped in better understanding of the processes for their fruitful application to real time requirements.

The branch of Radiochemistry and Nuclear Chemistry was relatively new to Indian Universities and it was essential to make special efforts to popularize this branch. The radiochemists from BARC took active part over the past 40 years in conducting a large number of collaborative programmes with universities. Under the auspices of Indian Association of Nuclear Chemists and Allied Scientists (IANCAS), supported by BRNS, DAE, Radiochemistry and Fuel Chemistry Division staff members

also organized a large number of workshops for teaching this subject to university teachers, and research students. The programme of this education activity is also extended to the high schools.

Summary

After five decades of continuous research and development activities in the Fuel Chemistry and Radiochemistry Programme of DAE, perhaps it is not too immodest to feel proud

that the Programme could fulfill the dreams of its founders and has enough confidence and is ready to take on fresh challenges to meet the future requirements of the Department. The Programme will continue to play a vital role to address many of the issues related to chemical and physico-chemical aspects of thorium based fuel technology thus fully utilizing country's vast resources of thorium to satiate the ever increasing energy demands to realize a self-sufficient and prosperous India.