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BARC Scientists Honoured
From the Editor’s Desk

The second issue of the BARC Newsletter for this year features five articles and two Brief Communications.

Two articles of general interest on characterization of nuclear materials are described in detail. One of the articles showcases recent developments in Nuclear Analytical Techniques (NATs), particularly neutron activation analysis (NAA) and (ii) prompt gamma ray NAA (PGNAA) utilizing neutron and proton based nuclear reactions. These techniques are useful in the chemical characterization of various materials at major to trace concentration levels. The other article deals with Total Reflection X-ray Fluorescence (TXRF), an advanced variant of Energy Dispersive X-ray Fluorescence (EDXRF), which is an important technique of material characterization.

BARC has designed and developed the advanced telecobalt unit, Bhabhatron-II, which has been successfully deployed across India. High specific activity cobalt-60 sources are required for these machines. One of the secondary sources of cobalt, spent ammonia cracker catalyst (SACC) has been investigated for the production of cobalt shapes. The entire process for extracting cobalt from the SACC and its conversion to cobalt powder and finally to nickel plated shapes of the specified shapes has been described in another article.

In addition to the above, the BARC Newsletter is proud to inform about the Padma Shri Award conferred by the President of India on Shri Sekhar Basu, Director, BARC and Dr. R.B. Grover, Dean, HBNI in March this year.

Dr. K. Bhanumurthy
On behalf of the Editorial Committee
Redox Reactions in Nanoscale Confinement

(Radiochemistry & Isotope Group)

Materials confined at the atomic scale exhibit unusual properties due to nanoconfinement effect. Chemistry in a confined nanospace may thus be different from that of bulk system. We have demonstrated for the first time the intrinsic role of nanoconfinement in facilitating the chemical reduction of metal ion precursors with a suitable reductant for the synthesis of metal nanoparticles, when the identical reaction does not occur in bulk solution. Taking the case of citrate reduction of silver ions under the unusual condition of [citrate]/[Ag+] > 1, it has been observed that the silver citrate complex, stable in bulk solution, decomposes readily in confined nanodomains of charged and neutral matrices (ion-exchange film and porous polystyrene beads), leading to the formation of silver nanoparticles. 1 It has been experimentally observed that the nanoconfined redox decomposition of silver citrate complex is responsible for the formation of Ag seeds, which thereafter catalyze oxidation of citrate and act as electron sink for subsequent reduction of silver ions. At present, there is no scheme for in situ formation of Ag nanoparticles using Ag+ ions in anion-exchange and neutral matrices. The Ag nanoparticles thus formed are uncapped, stable and easily accessible through interconnected pores or channels in the matrices. The easy retrieval of the matrix supported nanoparticles from the systems makes them reusable nanocatalysts without contaminating the products and system.

Formation of Ag nanoparticles in anion-exchange membranes as a function of reduction time, and in neutral nanoporous Amberlite XAD-4 beads. In all these host matrices, the nanopores or nanoconfinements are of the order of 5 nm.

1. Langmuir 2014, 30, 2460-2469
Development of Nano Magnetite Film on Carbon Steel

(Chemistry Group)

Magnetite with spinel structure forms as protective oxide film on the internal surfaces of the Primary heat transport system of PHWRs during Hot-conditioning. The surface is passivated with ferrite film formed by circulating high temperature water (250-260°C) under alkaline condition with low dissolved oxygen which is called as “Hot-conditioning”. Protection of internal surfaces against corrosion can be further improved by having a passive film containing nano crystallites. A method has been developed for forming a magnetite film with nano crystallites on carbon steel surfaces and its corrosion protection properties were studied. Polyethylene glycols are stable under the hot-conditioning process conditions. Different molecular weights and concentrations of polyethylene glycols were tested for getting oxide film with nano crystallites on the carbon steel surface at 250 °C. Polyethylene glycol with molecular weight 8000 and a concentration of 1g/L showed particle size reduction by a factor of ~10 (Fig.). No change in the oxide phase and morphology of nano crystallites (<100nm) was observed. The electrochemical characterization of these films showed an increase in the resistance values by a factor of 2. The oxide film formed on carbon steel under modified hot-conditioning procedure and normal hot conditioning procedure were tested under simulated reactor operating water chemistry conditions. The results showed a decrease in the corrosion rate and metal release rate for the oxide film with nano crystallites magnetite film on CS compared to microcrystalline magnetite film. Further work on removal of organics is in progress.

Fig.: SEM of magnetite particles over the carbon steel surface formed under two different conditions
Introduction

Total reflection X-Ray Fluorescence (TXRF) is a comparatively new technique of material characterization and trace element analysis. It is an advanced variant of Energy Dispersive X-ray Fluorescence (EDXRF) and is based on the principle of total reflection of X-rays when these radiations fall on a flat smooth surface at a grazing angle less than the critical angle of the sample support. The critical angle is in the range of about 0.1-1 degree in most cases. For TXRF analysis, a few microlitres of sample solution is deposited and dried on a flat sample support to make a thin film specimen and irradiated with X-rays in total reflection condition. As the X-rays do not penetrate inside the sample support in this condition, there is very little scattering of the X-rays from the sample support and, therefore, the background is considerably reduced. In addition, the specimen is excited by incoming as well as the totally reflected beam. This condition makes the excitation efficiency of the elements almost double compared to the conventional X-Ray Fluorescence (XRF). Moreover, since the detector can be placed very near to the sample, at an angle of 90 degrees with respect to the sample support, the solid angle subtended by the detector over the sample increases. These three important factors i.e. 1. Low background, 2. Double excitation of the specimen by the X-rays and 3. Proximity of the detector to the specimen, contribute towards achievement of better detection limits in the range of ng/mL level with a sample size of a few microlitres in TXRF [1-5]. In addition, the matrix effect, which is very troublesome in EDXRF, is minimized in this condition as the sample thickness is in a few nanometer range only. This makes TXRF technique universal not requiring matrix matched standards. The difference in instrumentation in EDXRF and TXRF is shown in Fig. 1.

The analytical capability of TXRF was first recognized in 1971 by two Japanese scientists Yoneda and Horiuchi [1]. Since then, the technique is being increasingly used in various scientific areas e.g. Chemistry, Physics, Environmental Sciences, Geology, Biology, Material science, Medicine, Forensics, Archaeology, Art and History, etc. It finds mainly three main types of applications: 1. Trace element...
analysis 2. Micro analysis and 3. Depth profiling [1-2, 5]. For trace and micro analysis, about 10 μL of the sample in solution form is deposited on a quartz or any other suitable material sample support, dried and TXRF spectrum is recorded. The elemental concentrations are determined by comparison of the normalized intensities of each element after consideration of its characteristic X-ray line sensitivity with that of an internal standard mixed previously in the sample. Since this technique requires very small amount of sample (picogram to nanogram level of analyte on the sample support), has multielement analytical capability, can analyze metals and non-metals alike and is sample non-consumptive, it is very much suited for the trace element determination in nuclear materials which are often radioactive. All these features result in minimizing the generation of radioactive waste, saving of precious nuclear materials and less dose to the analyst as well as the instrument when this technique shall be used for analysis of radioactive samples.

A TXRF spectrometer was procured and installed in Fuel Chemistry Division, in November 2003 for characterization of nuclear materials. Since then, this instrument has been used to develop TXRF methodology for application in different areas of nuclear material characterization. This spectrometer has been used for trace element analysis: metallic as well as non-metallic in uranium, thorium and plutonium oxides and carbides, major element determinations in mixed uranium-thorium oxide matrices, certification of presence of indium at level < 1 ng/mL in heavy water, determination of uranium in sea water and other type of waters, forensic and environmental sample analysis. Some of the results obtained in these studies are reported in the present article.

Instrumentation

An ITAL STRUCTURES TXRF spectrometer: TX-2000 was used in these studies. The spectrometer is equipped to use single or dual target X-ray tubes for sample excitation. For most of the experiments a Mo-W dual target tube was used. Such dual target tubes can be tuned to allow either Mo Kα, Kβ, W Lα or W Lβ beams to fall on sample for excitation without changing the X-ray tube. Mo Kα can efficiently excite medium and high atomic number elements K and L lines respectively and W Lα/β can excite K lines of low Z elements. Mo Kβ has low intensity but can be useful for elements e.g. Nb. A W-C multilayer with 2d = 49.4 Å was used to monochromatize the incident radiation emitted from the X-ray tube so that a particular energy e.g. Mo Kα / Kβ or W Lα / Lβ can be used for sample excitation. The spectrometer generator is usually operated at voltage and current of 40 kV and 30 mA, respectively. The sample chamber has the capability to measure twelve samples in one loading sequentially. Polished quartz sample supports of 30 mm diameter and 3 mm thickness were used as sample carriers. The characteristic X-rays emitted from the sample are detected with a Si (Li) detector having a resolution of 139 eV (FWHM) at 5.9 keV (Mn Kα). The X-ray spectra were acquired and processed.
Calibration and validation

In TXRF analysis, the elemental quantification is very simple due to negligible matrix effects and can be done by adding an internal standard to the sample solution. After thorough mixing of these solutions, a few microlitre aliquots of the sample solutions are deposited on the sample supports. The sample supports are flat polished surface normally made of Quartz, Plexiglas, Gold, etc. For the calibration of the spectrometer we used MERCK ICP- multielement standard (MES) solution IV. This standard contains 23 elements having elemental concentrations of 1000 mg/L and was diluted in suprapure nitric acid to bring the concentration of the elements to a few µg/mL levels. A TXRF spectrum of such standard with elemental concentration of 5 µg/mL and a sample size of 10 µL deposited on quartz sample support is shown in Fig. 2. The net intensities of all the elemental X-ray lines in MES were calculated by finding the area under the peak for each element using TXRF data processing program EDXRF32. The absolute sensitivities were calculated by taking the ratio of net intensity to concentration. The relative sensitivities with respect to internal standards were calculated by dividing the absolute sensitivity of each element with the absolute sensitivity of the internal standard. In TXRF analysis, relative sensitivity values are used for quantification because it is very difficult to make specimens of same area and thickness being exposed to incoming X-rays in reproducible geometry in each measurement. The benefit of using relative sensitivity values is that the change in X-ray intensities due to different area and sample amount being exposed do not cause errors in quantification, as this type of measurement shall not result in change in relative sensitivity value whereas it may change the absolute sensitivity value. The relative sensitivity values are constant for a particular spectrometer with fixed instrumental parameters. The quantification is done using the equation:

\[
C_x = \frac{N_x}{N_{IS}} \cdot \frac{S_{IS}}{S_x} \cdot C_{IS}
\]  

(1)

where, \(C_x\) is the concentration of the analyte present in the sample, \(N_x\) and \(N_{IS}\) are the net intensities of analyte X-ray lines being used for the analysis and that of internal standard respectively, \(S_x\) and \(S_{IS}\) are the relative sensitivities of the analyte and internal standard elemental X-ray lines and \(C_{IS}\) is the concentration of internal standard.

Before applying this technique for trace element determinations in nuclear materials, it was validated by analyzing a diluted MERCK ICP- multielement standard (MES) solution IV having elemental concentrations of 900 ng/mL. The analytical results obtained with Ga as internal standard are shown by a bar graph in Fig. 3. Using the TXRF spectrum of above standard, the detection limits were also determined for sample volume of 10 µL and 1000s measurement time employing the formula:

\[
DL = \frac{\text{Concentration}}{\text{Peak Area}} \cdot 3 \cdot \sqrt{\text{Background Area}}
\]  

(2)

Fig. 2: TXRF spectrum of a MERCK ICP- multielement standard (MES) solution IV diluted to 5 µg/mL. The spectrum was measured using Mo Kα excitation. X-ray tube was operated at 40 kV, 30 mA and counting time used was 1000 s.
where DL is the detection limit. The typical detection limits obtained were 137 ng/mL for Al (1.37 ng absolute) and 3 ng/mL (30 pg absolute) for Sr. A plot of detection limit vs. atomic number is shown in Fig. 4. Preconcentration of the analyte by some suitable technique e.g. solvent extraction, volume reduction by evaporation of the solvent, etc. improves the detection limits by several orders of magnitude.

**Trace metallic determinations in uranium and thorium oxide standards**

Applicability of TXRF for the trace metallic determinations in uranium and thorium oxides was studied in our laboratory. Trace metallic impurities which get incorporated into the nuclear fuel material during various fuel fabrication operations viz. milling, crushing, grinding, dissolution, pelletization, etc., not only affect their properties and performance but also lead to decrease in the total fissile content. Hence their determination is an important part of chemical quality assurance. For TXRF determinations in uranium oxide Certified Reference Materials (CRMs), developed by our Department of Atomic Energy, samples were dissolved in suprapure nitric acid. The major matrix uranium was separated by solvent extraction using tri-n-butyl phosphate (TBP) and the trace elements remaining in the aqueous phase were determined by TXRF using Ga as an internal standard [6]. The TXRF spectrum of a processed uranium oxide CRM is shown in Fig.5. The applicability of TXRF for the trace element determinations in such uranium samples was demonstrated by good agreement in the TXRF determined and certified trace element concentrations. In addition, our laboratory participated in an Inter- Laboratory Comparison Experiment (ILCE) conducted by our Department of Atomic Energy to develop certified reference materials (CRM) for trace metallic elements in thorium oxide [7]. The trace elements in thorium oxide samples were determined in same way as used for uranium oxide analysis. The TXRF results obtained in this ILCE were in very good agreement with the other trace element analytical techniques e.g. ICP-AES, ICP-MS and AAS from different laboratories and were helpful in the development of these samples as CRMs of thorium.
oxide. A comparison of the certified concentrations of trace elements in these CRMs and respective TXRF determined values are shown in Table 1. The good agreement in these values gave us confidence about the applicability and potential of TXRF for trace element (above Z=13) determinations in uranium and thorium using air as ambient atmosphere.

Fig. 5. TXRF spectrum of a processed uranium oxide standard (CRM-1) containing Ca = 63, Cr = 28, Cu = 26, Mn = 31 and Ni = 25 μg/g after matrix separation

Trace non-metallic determinations in nuclear materials

Though TXRF can analyze metals and non-metals alike, some elements require special treatment of the sample before these can be analyzed by TXRF. Chlorine is one such element. Normally chlorine is determined as chloride by Ion Chromatography (IC). For such determinations of chlorine in nuclear materials, it is first separated from the main matrix using pyrohydrolysis. The evolved chlorine, obtained after pyrohydrolysis, is collected in an acidic buffer. However when such solution containing Cl was mixed with Co internal standard and a few microlitres of the solution were deposited on quartz supports and TXRF spectra were measured using W Lα as excitation source, the TXRF spectra did not show any Cl Kα peak. This was due to the fact that when solution containing chlorine in acidic medium was dried on the sample supports, the chlorine is driven out as HCl. In order to avoid such loss of chlorine in TXRF determination in nuclear materials e.g., uranium, thorium, plutonium oxides and carbides, the pyrohydrolysis methodology was modified by collecting the evolved chlorine in 5mM NaOH solution. This solution was mixed with Co internal standard in basic medium. The TXRF spectrum of the specimen prepared by such modified methodology showed clear Cl Kα peak. The TXRF determined Cl concentrations were compared with IC determined Cl determinations. It was found that the TXRF results were comparatively less accurate and precise. This may be because Cl Kα, especially when Cl is present in trace amounts, has interference with Ar Kα peak coming from the presence of Ar in atmosphere. In order to countercheck this problem, TXRF measurements were made using Helium purge on the TXRF supports in such a way that path between the sample and the detector is filled with helium during TXRF measurements. This resulted in elimination of Ar Kα peak (as shown in Fig. 6) and improved the precision and accuracy of Cl determinations by TXRF. Using this approach, the agreement in TXRF determined and IC determined chlorine concentrations [8] could be improved. This method of Cl determination has the advantage that it avoids the process of cumbersome sample dissolution and requirement of putting the spectrometer inside the glove box for radioactive samples. The TXRF spectrum of a pyrohydrolysed condensate obtained from a PuO₂ sample and measured using helium purge is shown in Fig. 7. The agreement in TXRF and IC determined concentrations of Cl in some samples is shown in Table 2. In addition, we have developed TXRF method for sulphur determination in uranium matrix with good agreement in expected and TXRF determined sulphur concentrations [9].

Determination of indium in heavy water sample

Heavy water is used as a coolant and moderator in pressurized heavy water reactors. This water should be free from even ultra trace level of elements which produce highly radioactive isotopes after neutron absorption as this will create radiation exposure risk to personnel working in reactor area. Indium is one such element. It produces ¹¹⁶Inₐ isotope after neutron absorption. ¹¹⁶Inₐ has half-life of 54 minutes and emits γ rays of energy > 1MeV. One of the heavy water samples was to be certified to contain indium at a level < 1 ng/
mL. TXRF conditions were modified to excite In $K\alpha$ (24.21 keV) using a continuum strip (28-35 keV) obtained from the X-ray tube operated at 50 kV and 20 mA with the help of proper selection of multilayer angle. In addition, the sample was preconcentrated by evaporation of 50 mL of heavy water to approximately 100 microlitres. Using this approach indium presence in the heavy water could be ruled out at a level of 1 ng/mL [10].

**Bulk determinations of uranium and thorium in nuclear materials**

Apart from trace determinations, bulk characterization of nuclear materials, specially the mixed oxides, is an important part of chemical quality assurance. Studies to assess the applicability of TXRF as a micro analytical technique for the bulk determinations of uranium and thorium in solution samples were made [11]. These samples were analyzed in similar way as used for trace element determinations but the samples were diluted to a total matrix concentration of < 1000 mg/L so that matrix effect does not affect the results.

For solid sample analysis of (U, Th)O$_2$ in the form of pellets (sintered as well as green), microspheres and powders, a simple method of TXRF determination of major elements was developed. The TXRF sample support was gently rubbed with these samples so that a few ng samples are transferred on the support. The TXRF spectrum was measured and uranium was determined with respect to thorium (or vice versa). Fig. 8. shows a TXRF spectrum of a (U, Th)O$_2$ pellet measured using a specimen obtained after rubbing the sintered pellet gently on quartz sample support.

### Table 1: Comparison of TXRF determined elemental concentrations of some elements with the certified values in thorium oxides CRMs (all values in $\mu g/g$)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Th$_2$O$_5$</th>
<th>Th$_2$O$_4$</th>
<th>Th$_2$O$_3$</th>
<th>Th$_2$O$_3$-MOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>ND</td>
<td>-</td>
<td>0.70</td>
<td>ND</td>
</tr>
<tr>
<td>Ca</td>
<td>67</td>
<td>73</td>
<td>0.92</td>
<td>784</td>
</tr>
<tr>
<td>Co</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Cr</td>
<td>4.5</td>
<td>0.6</td>
<td>0.3</td>
<td>14.6</td>
</tr>
<tr>
<td>Cu</td>
<td>1.9</td>
<td>3.1</td>
<td>0.61</td>
<td>93</td>
</tr>
<tr>
<td>Fe</td>
<td>46</td>
<td>8</td>
<td>0.82</td>
<td>122</td>
</tr>
<tr>
<td>K</td>
<td>7.3</td>
<td>0.9</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Mn</td>
<td>2.4</td>
<td>0.2</td>
<td>0.80</td>
<td>7</td>
</tr>
<tr>
<td>Ni</td>
<td>7.7</td>
<td>0.6</td>
<td>0.11</td>
<td>0.70</td>
</tr>
<tr>
<td>Pb</td>
<td>0.5</td>
<td>0.2</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>Sr</td>
<td>0.28</td>
<td>0.08</td>
<td>-</td>
<td>1.63</td>
</tr>
<tr>
<td>V</td>
<td>ND</td>
<td>-</td>
<td>0.21</td>
<td>7</td>
</tr>
<tr>
<td>Y</td>
<td>ND</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>0.7</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

| SD: Precision in terms of standard deviation (1 s) of four TXRF determinations. TX: TXRF determined; Cer*: Certified values; ND: Not detected; NR: Not reported.

### Table 2: Comparison of TXRF and IC determined chlorine concentrations in Pyrohydrolysis condensates of plutonium oxide and alloy samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>TXRF* (µg/mL) (A)</th>
<th>IC# (µg/mL) (B)</th>
<th>(A/B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide-1</td>
<td>3.43 ± 0.08</td>
<td>3.36 ± 0.02</td>
<td>1.02</td>
</tr>
<tr>
<td>Oxide-2</td>
<td>12.0 ± 0.2</td>
<td>10.3 ± 0.14</td>
<td>1.17</td>
</tr>
<tr>
<td>Oxide-3</td>
<td>2.26 ± 0.09</td>
<td>2.33 ± 0.02</td>
<td>0.97</td>
</tr>
<tr>
<td>Oxide-4</td>
<td>2.5 ± 0.4</td>
<td>3.01 ± 0.01</td>
<td>0.82</td>
</tr>
<tr>
<td>Oxide-5</td>
<td>1.8 ± 0.1</td>
<td>2.12 ± 0.01</td>
<td>0.85</td>
</tr>
<tr>
<td>Alloy-1</td>
<td>112 ± 15</td>
<td>95.64 ± 0.66</td>
<td>1.17</td>
</tr>
<tr>
<td>Alloy-2</td>
<td>66.05 ± 1.16</td>
<td>80.71 ± 0.35</td>
<td>0.82</td>
</tr>
</tbody>
</table>

**Table 2:** Comparison of TXRF and IC determined chlorine concentrations in Pyrohydrolysis condensates of plutonium oxide and alloy samples.
and presenting it for TXRF measurements. The advantages of this method are the requirement of very small sample amount (in nanogram range) for analysis and negligible sample preparation and almost non-destructive sample analysis. The precision obtained was better than 2% in both the solution and the solid samples. The deviation of the TXRF determined values from the expected values for most of the cases was less than 2%. This study initiated a new kind of application of TXRF as a micro analytical technique for the bulk determination of constituents in radioactive samples.

Conclusions

Applicability of TXRF for trace as well as bulk determinations in nuclear materials was successfully demonstrated. The studies have established that TXRF, an upcoming technique for trace element determination, is not only comparable but better in certain aspects e.g. non-consumption of the sample, low operating cost, multielement analytical capability including metals and non-
metals, no memory effect, negligible matrix effect, analysis of almost all the elements from Z=11 (Na) using lab source, compared to most of the conventional trace determination techniques. For low atomic number elements, Vacuum Chamber TXRF is advantageous. For radioactive materials, it has an added advantage that it requires very less amount of sample and produces negligible waste and this saves unnecessary radioactive exposures to the working personnel, poses less problem of radioactive waste management and saves precious nuclear materials from wastage. The new developments in TXRF e.g. vacuum chamber based TXRF, TXRF-XANES/EXAFS, Total Reflection XPS, when applied to nuclear materials, shall not only cover almost whole periodic table for elemental determination but also be able to give additional information e.g. speciation, atomic environment, etc.

Acknowledgements:

The authors express their sincere thanks to all co-authors of various publications included in this article.

References:

Chemical Characterization of Materials Relevant to Nuclear Technology Using Neutron and Proton Based Nuclear Analytical Methods

R. Acharya
Radiochemistry Division

Abstract:
Nuclear analytical techniques (NATs), utilizing neutron and proton based nuclear reactions and subsequent measurement of gamma rays, are capable of chemical characterization of various materials at major to trace concentration levels. The present article deals with the recent developments and applications of conventional and \( k_{\text{eff}} \)-based internal monostandard (i) neutron activation analysis (NAA) and (ii) prompt gamma ray NAA (PGNAA) methods as well as (iii) in situ current normalized particle induced gamma ray emission (PIGE). The materials that have been analyzed by NAA and PGNAA include (i) nuclear reactor structural materials like zircaloy, stainless steels, Ni alloys, high purity aluminium and graphite and (ii) uranium oxide, U-Th mixed oxides, uranium ores and minerals. Internal monostandard NAA (IM-NAA) method with \textit{in situ} detection efficiency was used to analyze large and non-standard geometry samples and standard-less compositional characterization was carried out for zircaloy and stainless steels. PIGE methods using proton beams were standardized for quantification of low Z elements (Li to Ti) and applied for compositional analysis of borosilicate glass and lithium titanate (Li\(_2\)TiO\(_3\)) samples and quantification of total B and its isotopic composition \((^{10}\text{B}/^{11}\text{B} \text{ atom ratio})\) in boron based neutron absorbers like B\(_4\)C.

Introduction
Chemical characterization of materials is the first and most important step in chemical quality control (CQC) exercise, which involves determination of major, minor and trace elements with good accuracy and precision. CQC provides a means to ensure the quality of the fabricated material as per the required chemical specifications. In the case of reactor materials, the finished products should meet the stringent chemical specifications for major to trace constituents, since they affect the material properties as well as performance under prevailing operating conditions. Besides major and minor constituents, knowledge of concentrations of trace elements like H, B, Cl, rare earth elements (REEs) and neutron poisons like Cd and Gd is essential to establish the suitability of the materials. The materials of interest are mainly nuclear fuels and structural materials of existing as well as upcoming Indian research and power reactors. It is important to use suitable analytical techniques to analyze these complex matrices (alloy, oxide, carbide and ceramics) and obtain good quality results. Routinely used analytical methods are mostly wet chemical (classical), chromatographic (IC and HPLC) and, atomic and mass spectroscopic techniques (AAS, ICP-AES and ICP-MS). Though these techniques give high quality results at low concentration levels, they are destructive methods and thus not free from reagent blank corrections and they experience matrix effect. In some cases, radio/nuclear analytical techniques like alpha and gamma-ray spectrometry, XRF, neutron activation analysis (NAA) and ion beam analysis (IBA) are used. Nuclear analytical techniques (NATs) namely NAA, prompt gamma-ray NAA (PGNAA) and particle induced gamma-ray emission (PIGE) are isotope specific techniques and have several advantages like simultaneous multielement determination, non-destructive in nature, negligible matrix effect, high sensitivity and selectivity, and inherent precision and accuracy. Instrumental NAA (INAA) using reactor neutrons is a good technique for medium and high Z elements, whereas PGNAA, an on-line measurement technique, is suitable for...
low to high Z elements including H and neutron poisons. On the other hand, PIGE, which is also an on-line technique, is capable of determining low Z elements from Li onwards including Be, B, C, N, O and F. Present article deals with developments and applications of such NATs to materials relevant to nuclear fuel cycle.

Principle of Neutron Activation Analysis (NAA)

When a target isotope of an element is exposed to neutrons, a compound nucleus (CN) is formed in the excited state. The CN decays to lower energy ground state by emitting gamma rays promptly (10^{-12} to 10^{-13}s) which are called prompt γ-rays and intensity of these γ-rays is directly proportional to isotopic (elemental) concentrations. This on-line measurement technique is called prompt gamma-ray NAA (PGNAA). The CN in the ground state decays often by emitting a β- particle and the product formed is an isotope of another element that de-excites to ground state by emitting characteristic (delayed) gamma rays. In conventional NAA, intensity of these γ-rays is measured. PGNAA and NAA are schematically represented in Fig. 1 (Ref. www.iki.kfki.hu/nuclear/research).

![Fig. 1: Interaction of neutrons with target isotope and production of prompt and delayed gamma rays](image)

The activity produced in NAA at the end of irradiation period (t_i) is given by,

\[ A = N \sigma \phi (1-e^{-\lambda t_i}) \]  

(1)

N is the number of target atoms, \( \sigma \) is the \((n,\gamma)\) capture cross section in barn (cm^2), \( \phi \) is the neutron flux (cm^-2 s^-1) and \( \lambda \) is the decay constant (s^-1) of the activation product. Concentrations are calculated by relative or single comparator method.

Single comparator \((k_0)\) methods of NAA and PGNAA

Routine work using conventional NAA is carried out by relative method. It is a ratio method where elemental concentrations are calculated with respect to the standards used. On the other hand, \(k_0\)-based NAA uses a single comparator like ^197Au or any other suitable element [1-4] that is co-irradiated with the sample. As the single comparator is different than the element of interest, this method needs neutron spectrum parameters, detection efficiency and \(k_0\) factor [4] for concentration calculation. The \(k_0\) method is advantageous in PGNAA, as sample and standard can’t be co-irradiated together in on-line measurement [5]. Though routine work is carried out using small size samples (10-500 mg), large size sample (g-kg scale) analysis is advantageous as it provides better analytical representativeness. When the \(k_0\)-based NAA method is applied to samples of large size as well as non-standard geometry samples, neutron flux perturbation during sample irradiation and γ-ray self-attenuation during measurements need to be considered. These issues have been taken care in \(k_0\)-based internal monostandard NAA (IM-NAA) method using in-situ relative detection efficiency [6-8]. The \(k_0\)-NAA method was adapted in the year 1995 and \(k_0\)-PGNAA method using neutron beam facility at Dhruva research reactor was optimized in 1999 in BARC. Later in 2003, IM-NAA was developed to deal with large and non standard geometry samples. Details of conventional and \(k_0\) methods in NAA and PGNAA, developments, validation and applications to various samples including nuclear materials can be found in our publications [3, 7, 8, 10-29] and some of the salient results are given here.

Experimental

Neutron spectra of irradiation positions of reactors were characterized by determining epithermal neutron flux shape factor (\(\alpha\)) using multi-monitors of Au, Zr, In, Mo and Zn. Sample masses used were...
10 mg to 0.5 kg and durations of irradiation were 1 min to 1 day. Radioactivity was assayed using HPGe detector based gamma ray spectrometers. On-line measurements in PGNAA were carried out using a Compton suppressed spectrometer consisting of 40% HPGe detector with BGO shield. Peak areas were evaluated by peak-fit method using the PHAST software, developed at BARC [9]. Details of concentration calculations including efficiency calibrations are found in references 7, 8 and 28.

**Concentration calculation in k\(_0\) based NAA and PGNAA**

In the k\(_0\)-NAA and IM-NAA [3,7], the ratio of mass (m) of an element (x) to the mass of the comparator element (y) in the sample is given by Eq. (2)

\[
m_{x}/m_{y} = \frac{(S.D.C)(f + Q_{\alpha}(\alpha))_{x} \cdot P_{A_x} \cdot \epsilon_x}{(S.D.C)(f + Q_{\alpha}(\alpha))_{y} \cdot P_{A_y} \cdot \epsilon_y \cdot k_{0,H}(x)/k_{0,H}(H)}
\]

where \(P_{A_x}\) is the net peak area under the gamma ray peak of interest, S is the saturation factor \((1-e^{-t})\), D is the decay factor \((e^{-t})\), C is the term used for correcting the decay during counting period and is given by \(((1-e^{-LT})/\lambda LT)\), ti, tc and LT are time durations of irradiation, cooling and counting respectively, f is the sub-cadmium to epithermal neutron flux ratio, \(Q_{\alpha}(\alpha)\) is the ratio of the resonance integral \((I_{R})\)-to-thermal neutron cross section \((\sigma_{\alpha})\) corrected for \(\alpha\). \(\epsilon\) is the absolute detection efficiency and \(k_{0,H}\) is the literature recommended k\(_0\)-factor [4]. In k\(_0\)-based PGNAA, calculation of mass ratio [5] is similar to IM-NAA and simpler as saturation and decay factors are not input parameters.

\[
m_{x}/m_{y} = \frac{P_{A_x}}{P_{A_y}} \cdot \frac{\epsilon_x}{\epsilon_y} \cdot \frac{k_{0,H}(x)}{k_{0,H}(H)}
\]

where \(k_{0,H}\) is literature prompt k\(_0\)-factors with respect to H [5]. From the concentration ratio, absolute concentration is obtained. In both IM-NAA and IM-PGNAA, efficiency ratios, instead of absolute efficiencies, are sufficient for concentration ratio calculations [6, 7].

**Results and discussion**

Table 1 gives the neutron spectrum/flux parameters namely epithermal neutron shape factor \((\alpha)\), sub-cadmium to epithermal neutron flux ratio \((f)\), % thermal neutron component and neutron flux values (at 50% of maximum operating power) of reactors [10-12].

### Table 1: Neutron spectrum/flux parameters of irradiation positions of research reactors

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Position</th>
<th>(\alpha)-value</th>
<th>(f = \phi_{uv}/\phi_{e})</th>
<th>%(n_{th})</th>
<th>Flux (n cm(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apsara</td>
<td>E8</td>
<td>0.0355±0.0059</td>
<td>49.8±1.4</td>
<td>98.0</td>
<td>5x10(^{11})</td>
</tr>
<tr>
<td></td>
<td>Thermal Column</td>
<td>NA</td>
<td>6.0x10(^{3})</td>
<td>99.98</td>
<td>1.2x10(^{8})</td>
</tr>
<tr>
<td>CIRUS</td>
<td>Self Serve</td>
<td>0.011±0.001</td>
<td>80.0±3</td>
<td>98.7</td>
<td>3x10(^{13})</td>
</tr>
<tr>
<td>PCF</td>
<td></td>
<td>0.010±0.001</td>
<td>120±4</td>
<td>99.2</td>
<td>3x10(^{13})</td>
</tr>
<tr>
<td>AHWR CF</td>
<td>Graphite Reflected</td>
<td>NA</td>
<td>8.6x10(^{2})</td>
<td>99.9</td>
<td>3.4x10(^{7})</td>
</tr>
<tr>
<td>Dhruva</td>
<td>Reflected beam</td>
<td>NA</td>
<td>4.2x10(^{7})</td>
<td>99.98</td>
<td>1.4x10(^{6})</td>
</tr>
<tr>
<td>PCF</td>
<td></td>
<td>NA</td>
<td>35.0±1.5</td>
<td>97.2</td>
<td>5x10(^{13})</td>
</tr>
<tr>
<td>KAMINI</td>
<td>PFTS</td>
<td>-0.0406±0.0025</td>
<td>25.1±0.4</td>
<td>96.2</td>
<td>5x10(^{11})</td>
</tr>
</tbody>
</table>
Quality Assurance/Quality Control (QA/QC)

Under QA/QC work, $k_{\text{eff}}$-NAA method was validated by determining concentrations of about 30 elements in many (certified/standard) reference materials (RMs) namely USGS W-1 and NOD-1, IAEA RMs Soil-7 and SL-3 and NIST SRM 1571 [13]. For validation of IM-NAA, SMELS (I-III) from IRMM and IAEA RMs SL-3 and Soil-7 and BCS CRMs 225/1 (low alloy steel) and CRM 466 (austenitic SS) and NIST SRM 247 (high Ni alloy) [8,16] were analyzed. The % deviations were in the range of ±0.5-10% from certified/recommended values and the Z-score values (at 95% CL) were within ±1 for most of the elements.

Applications of IM-NAA

Large Sample NAA (LSNAA)

Analysis of a large and non-standard geometry object is a challenge for which an IM-NAA method was developed and successfully applied for the analysis of many nuclear reactor structural materials like zircalloys (zircaloy 2 and 4) [7, 15], stainless steels (SS 316M, D9 and SS 304L and BCS RMs) [7, 8, 16, 19], Ni – alloy [17] and high Ni SRM 247 [17], high purity aluminium clad [7,24] and uranium ores [18,19]. Photographs of some of the samples as received were activated and analyzed are shown in Fig. 2. A typical gamma ray spectrum of zircaloy 2 irradiated in Apsara thermal column is given in Fig. 3. The elements determined in

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration Specifications</th>
<th>Element</th>
<th>Concentration Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr%</td>
<td>98.2±0.7</td>
<td>Balance</td>
<td>Fe%</td>
</tr>
<tr>
<td>Sn%</td>
<td>(15.8±0.3)x10$^{-1}$</td>
<td>1.2-1.7</td>
<td>Cr%</td>
</tr>
<tr>
<td>Fe%</td>
<td>(1.8±0.2)x10$^{-1}$</td>
<td>0.07-0.2</td>
<td>Ni%</td>
</tr>
<tr>
<td>Cr%</td>
<td>(8.3±0.1)x10$^{-2}$</td>
<td>0.05-0.15</td>
<td>Mo%</td>
</tr>
<tr>
<td>Ni%</td>
<td>(7.8±0.4)x10$^{-2}$</td>
<td>0.03-0.08</td>
<td>Mn%</td>
</tr>
<tr>
<td>In$^+$</td>
<td>(1.0±0.1)x10$^{-1}$</td>
<td>NA</td>
<td>Co$^+$</td>
</tr>
<tr>
<td>Co$^+$</td>
<td>6.8±0.1</td>
<td>20</td>
<td>As $^+$</td>
</tr>
<tr>
<td>Ta$^+$</td>
<td>16.3±1.1</td>
<td>200</td>
<td>W $^+$</td>
</tr>
<tr>
<td>Hf$^*$</td>
<td>24.0±0.7</td>
<td>100</td>
<td>NA</td>
</tr>
<tr>
<td>Mn $^+$</td>
<td>10.7±0.1</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>As $^+$</td>
<td>4.5±0.4</td>
<td>NA</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Concentrations of elements in large size zircaloy 2 and small size D9-alloy by IM-NAA

a – concentration in mg kg$^{-1}$, NA – not available
Barc Newsletter

Research Article

Zircaloy samples are Zr, Sn, Fe, Cr, Ni, In, Mn, As, Co, W and Ta whereas in stainless steels, the determined elements are Fe, Cr, Ni, Mo, Mn, Co, As and W. The results of a zircaloy-2 and a D9-alloy are given in Table 2, where Zr and Fe were used as corresponding mono standards. Since all the major and/or minor elements in zircalloys and stainless steel samples are amenable to NAA, concentration values were obtained by standard-less approach. In the case of high purity (15-grade) aluminium, impurities (As, Fe, Ga, La, Mg, Mn, Na, Sc, Cr and Zn) could be determined with respect to aluminium mass as the mass of the sample was nearly due to Al. Uranium ore samples obtained from Jaduguda and Bhatin mines were analyzed for U, Th and REEs [18]. Four small (100 mg) and one large (56 g) size samples of two uranium ores were analyzed and results were found in good agreement, which validated LSNAA method [19]. The uranium concentrations were found to be in the range of 350-550 mg kg⁻¹. Results of two samples of uranium ore are given in Table 3 along with other samples.

Applications of relative method of INAA

Both thermal NAA (TNAA) and epithermal NAA (ENAA) methods were standardized to determine U and Th simultaneously in samples containing 4-30% U-Th oxides [20], where mixed oxide is the proposed fuel for Advanced Heavy Water Reactor (AHWR). Though in actual fuel ²³⁵U will be used, presently studies are carried out using natural U and Th mixed oxides. ENAA method with Cd filter was found advantageous, since gamma ray spectrum (Fig. 4) becomes simpler due to suppression of fission and activation products. Compton suppressed gamma ray spectrometry was used in ENAA to determine trace levels of Th (16-72 mg kg⁻¹) in uranium oxide (U₃O₈) samples and the values were in good agreement with those obtained by IC, ICP-AES and ICP-MS [21]. INAA and passive gamma ray spectrometry (PGS) were standardized for determination of U and Th in zircon & ilmenite minerals. U and Th concentrations values are given in Table 3. Small samples of nuclear grade graphite [22] and aluminium clad [23] were analyzed and concentration of eleven trace elements were determined. Low concentrations of

Table 3: U and Th concentrations (mg kg⁻¹) by INAA methods in various samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>U</th>
<th>Th</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Th mixed oxide</td>
<td>INAA</td>
<td>4.3±0.2</td>
<td>95.7±0.3</td>
<td>20</td>
</tr>
<tr>
<td>Uranium oxide</td>
<td>ENAA</td>
<td>-</td>
<td>16.2±0.8</td>
<td>21</td>
</tr>
<tr>
<td>U Ore-1</td>
<td>IM-NAA</td>
<td>463±9</td>
<td>9.7±0.3</td>
<td>18</td>
</tr>
<tr>
<td>U Ore-2</td>
<td>IM-NAA</td>
<td>358±4 (Large, N=1)</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>351±16 (Small, N=4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zircon</td>
<td>INAA</td>
<td>365±8</td>
<td>351±16 (Small, N=4)</td>
<td>-</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>INAA</td>
<td>21±1</td>
<td>203±4</td>
<td>-</td>
</tr>
</tbody>
</table>

![Fig. 4: Gamma-ray spectrum of 4% U-Th mixed oxide in ENAA](image-url)

![Fig. 4: Gamma-ray spectrum of 4% U-Th mixed oxide in ENAA](image-url)
Th (4-19 mg kg\(^{-1}\)) in soil samples [24] and U (2-3 mg kg\(^{-1}\)) in solid sorbents (used for extraction of U from sea water) [25] were determined by INAA. INAA method using pneumatic carried facility (PCF, Fig. 5) of Dhruva reactor was optimized for trace concentrations (9-575 mg kg\(^{-1}\)) of chlorine in zirconium based samples with a detection limit of 0.1 mg kg\(^{-1}\). PCF is immensely used for various NAA based R&D work using short-lived nuclides.

**Prompt Gamma-ray NAA (PGNAA)**

PGNAA facility was set up for the first time in India using neutron beam facilities at Dhruva reactor. As a part of QA program, prompt \(k_0\)-factors for isotopes of elements like H, B, N, Mg, Si, S, K, Ba, Cd, Sm, Hg and Gd were determined with respect to 1951 keV gamma-ray of \(^{36}\)Cl [26,27]. Several reference materials and samples like meteorites [28] were analyzed by \(k_0\)-PGNAA. Our lab participated in an IAEA inter lab comparison studies of a standard cement analysis using PGNAA and the results (Ca, Si, Fe, Al etc.) were in good agreement with the assigned values [29]. A methodology for correcting the self-shielding effect by neutron poisons like B, Cd and Gd was standardized and applied to samples containing high amount of B [30,31]. Boron was determined using 478 keV of \(^{10}\)B(n,\(\alpha\))\(^{7}\)Li. The developed method was used to determine elements B, Ti, Mo, Cr and Si in TiB\(_2\) alloy [30] and B in boron based chemical compounds and borosilicate glass samples [31]. Low concentrations of boron were determined in several RMs, with a detection limit of 1 mg kg\(^{-1}\) [31]. Results of boron concentrations in some samples are given in Table 4. PGNAA facility of the Budapest Research Reactor using cold-neutron beam was used for composition analysis of samples such as Zircaloys 2 and 4 and Zr-2.5% Nb alloy. The trace elements detected in general are B, Hf, Ti, Mn, Cl and Co [32]. Hydrogen concentrations in charged zircaloys were determined in the range of 26-287 mg kg\(^{-1}\) [33] utilizing 2223 keV prompt gamma ray from \(^1\)H (n,\(\gamma\))\(^2\)H reaction (Fig. 6).

### Table 4: Concentrations of B in various samples by PGNAA; (*Literature value of B)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Borosilicate glass (wt%)</th>
<th>TiB(_2) alloy (wt%)</th>
<th>Borax (wt%)</th>
<th>LaB(_6) (wt%)</th>
<th>SRM 1632a (mg kg(^{-1}))</th>
<th>SRM 1570a (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron Conc.</td>
<td>12.0±0.3</td>
<td>22.2±1.0</td>
<td>6.12±0.15</td>
<td>7.68±0.24</td>
<td>58.3±0.4</td>
<td><em>(58.7±0.7)</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><em>(37.6±1.1)</em></td>
</tr>
</tbody>
</table>
the work is carried out using thick targets in which the activity (A) produced is given by (4),

\[ A = N \times I \times \int_{E_0}^{E} \sigma(E) \, dE / S(E) \]  

(4)

where \( N \) is the number of target atoms, \( I \) is the beam current of particle of energy \( E \), \( \sigma(E) \) is the stopping power of the target and \( \sigma(E) \) is the charged particle induced nuclear cross-section at \( E \). The concentrations of elements \( (C_x = (CPS)_x / S, S \) is the elemental sensitivity) are determined using current normalized PIGE method. PIGE is a complementary technique to NAA, PIXE and XRF, and is capable of determining low Z elements like Li to Ca or higher Z using 2-9 MeV proton beams. Some of the PIGE reactions are listed in Table 5.

A PIGE facility has been set up at FOTIA, BARC (Fig. 8) as well as at BARC-TIFR pelletron. An in situ beam current normalized PIGE method has been developed and applied to borosilicate glass, lithium based ceramics like lithium titanate and boron based compounds [35-39], which are difficult to analyze by wet chemical/ conventional methods. Elemental standards as well as samples in pellet form (in cellulose or graphite) were irradiated using low energy proton beam (4 MeV) at FOTIA and IOP, and medium energy proton beam (8 MeV) at TIFR. Prompt gamma rays were measured using HPGe detector based high resolution spectrometers coupled to 8 k MCA. The PIGE spectra of lithium titanate and B,C are shown in Figs. 9 and 10, respectively. The PIGE method was applied for quantification of F and other constituents (Si, Al, Na and B) in barium borosilicate glass [34-36], which is a proposed nuclear waste vitrification matrix. Quantification F in glass will help in arriving at F retention / loss during vitrification process at high temperature conditions. Compositional analysis of sol-gel synthesized lithium titanate (a tritium breeder in fusion reactor under ITER) [37,38] was carried out for optimizing synthesis procedure as well as for CQC. Simultaneous quantification of Li, Ti and O contents could be done using 8 MeV proton beam [38]. Isotopic composition of B (\(^{10}B/^{11}B \) atom ratio) could be determined by PIGE in natural and enriched neutron absorbers including B,C using 429 and 718 keV of \(^{10}B \) and 2125 keV of \(^{11}B \) [39] in addition to total B concentrations.

<table>
<thead>
<tr>
<th>Element</th>
<th>Reaction</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>(^6)Li(p, \gamma)(^7)Be</td>
<td>429</td>
</tr>
<tr>
<td></td>
<td>(^7)Li(p, p'</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>(^7)Be(p, \alpha)(^4)Li</td>
<td>3526</td>
</tr>
<tr>
<td>B</td>
<td>(^{10})B(p, \alpha')(^7)Be</td>
<td>429</td>
</tr>
<tr>
<td></td>
<td>(^{10})B(p, p')(^{10})B</td>
<td>718</td>
</tr>
<tr>
<td></td>
<td>(^{11})B(p, p'</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>(^{12})C(p, p'</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>(^{14})N(p, p'</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>(^{16})O(p, p'</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>(^{19})F(p, p'</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>(^{23})Na(p, p'</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>(^{27})Al(p, p'</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>(^{28})Si(p, p'</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>(^{32})S(p, p'</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>(^{48})Ti(p, p'</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7: Principal of PIGE/PIXE

Table 5: Proton induced reactions of isotopes of low Z elements and prompt gamma-rays of interest in PIGE.

Fig. 8: PIGE setup at FOTIA, BARC
suppressed gamma ray spectrometry helped in achieving lower detection limits. PIGE method using proton beam was used to determine low Z elements (i.e., Li to Ti) and isotopic composition of B (10B/11B). Use of medium energy proton beam (7-10 MeV) would be useful for determination of low to medium Z elements including C, N, O, P and S. IBA including PIGE is complementary to NAA and PGNAA and thus further developments in PIGE will find immense applications for compositional characterization as well as trace element determination.

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Transgenic Approaches for Development of Disease Resistance in Banana

Upendra K. S. Shekhawat, Siddhesh B. Ghag and Thumballi R. Ganapathi
Plant Cell Culture Technology Section, Nuclear Agriculture & Biotechnology Division

Abstract

Banana (Musa spp.) is an important food and cash crop worldwide. Diseases and pests pose the most serious constraint to banana cultivation. Among the diseases, Fusarium wilt and banana bunchy top virus (BBTV) are the most important economically. We have explored different transgenic approaches for development of efficient resistance in banana against these two diseases. For countering Fusarium wilt, we have overexpressed Petunia floral defensins using a strong constitutive promoter in transgenic banana plants. We have also tested a host-induced gene silencing strategy targeting two vital fungal genes to obtain Fusarium resistant banana plants. For development of BBTV resistant banana plants also, we have used a host-induced gene silencing approach utilizing the full and partial coding sequence of the viral replication initiation protein. Successful bioassays performed in controlled greenhouse conditions have shown the efficacy of using these strategies to develop disease resistant banana plants.

Fusarium wilt of banana

Fusarium wilt (also called as the Panama disease) is the most important and devastating disease of banana. *Fusarium oxysporum*, which causes wilt disease in several crop plants, is known to be a soil borne ubiquitous species complex of plant pathogenic fungi that includes several *forme speciales*, each possessing a high degree of host specificity (Ploetz, 2006). *Fusarium oxysporum* f. sp. *cubense* (Foc) is the causal organism of Fusarium wilt of banana. Foc infects and subsequently occludes the xylem vessels of the banana roots leading to wilting and ultimately
death of the banana plant. Fusarium infected banana plants show progressive yellowing of leaves, cracking of the pseudostem and also discoloration of the corm tissue. As the fungus resides deep inside the plant in the xylem vessels, application of external fungicides is not effective in controlling Foc. Foc chlamydospores survive for decades in the soil, thereby making it permanently unsuitable for growth of healthy banana plants. Out of the four recognized races of Foc, race 1, which caused the epidemic in ‘Gros Michel’ plantations, also damages ‘Lady Finger’ (AAB) and ‘Silk’ (AAB) subgroups. Foc Race 2 infects cooking varieties like ‘Bluggoe’ (ABB) and race 4 can attack all known edible banana varieties including the ‘Cavendish’ (AAA) varieties (which are resistant to race 1) (Buddenhagen, 2009). Foc Race 4, presently is the biggest concern as it has now spread to the African continent also. As there are no natural sources of resistance available against Foc race 4 from any cultivated banana, the only option available is the development of Fusarium wilt resistance in elite banana varieties by genetic engineering. This is especially relevant to banana owing to its triploid nature and the parthenocarpic fruit development in most of the edible elite varieties.

In this direction, we have implemented a multidimensional approach towards engineering banana with efficient Fusarium wilt resistance. This includes the use of potent anti-microbial defensins with C-terminal prodomains like Petunia floral defensins as the initial first barrier to the Foc hyphal entry followed by host-induced gene silencing of vital fungal genes mediated by siRNAs during the intermixing of fungal and plant cytosol to ultimately prevent the prevention of programmed cell death in banana (possibly induced by Foc infection) by overexpression of select anti-apoptotic genes.

**Use of novel Petunia floral defensins for development of efficient resistance against Fusarium wilt in banana**

Antimicrobial peptides form a potent group of defense related proteins which have been used in development of resistance against a range of plant pathogens (Thomma et al., 2002). Defensins constitute one of the biggest families of these antimicrobial peptides in plants. Plant defensins, which generally possess 3-4 disulfide linkages, are particularly potent against fungal targets. Defensins target specific lipids on the fungal membranes thereby permeabilizing them to inhibit fungus growth. Floral defensins, derived from floral tissues of plants, have been demonstrated with potent growth inhibitory activity towards pathogenic filamentous fungi especially belonging to the *Fusarium oxysporum* species complex (Lay et al., 2003). In our laboratory, we amplified full length coding sequences of two *Petunia* floral defensins, *PhDef1* and *PhDef2* (having C-terminal 31 and 27 amino acids long prodomains) from *Petunia hybrida* floral tissues derived cDNA (Ghag et al., 2012). These were constitutively overexpressed in transgenic banana plants using embryogenic suspension culture cells as explants for *Agrobacterium*-mediated genetic transformation as described previously (Ganapathi et al., 2001). Efficient expression of these antifungal defensins in an elite banana cv. Rasthali resulted in significantly enhanced resistance against infection of *Fusarium oxysporum f. sp. cubense* in the transgenic plants as compared to equivalent controls as indicated by in *vitro* and *ex vivo* bioassays. Transgenic banana lines which were expressing any of the two ectopic defensins were seen to be less chlorotic and showed significantly less discoloration of the corm region of the banana plant as compared to untransformed controls (Fig. 1). Further these transgenic banana plants were phenotypically normal and no growth stunting was observed at any regeneration or growth stage. In contrast, another group of transgenic banana plants which constitutively expressed C-terminal truncated defensins (without the coding region for the pro-domains) were stunted from initial stages of regeneration and the corresponding transformation efficiency was also significantly less (Ghag et al., 2013). This indicated that expression of such potent defensin proteins without their cognate inactivating C-terminal pro-domains runs the risk of severely affecting the growth and development of the transgenic plants.
Host induced gene silencing (HIGS) of vital fungal genes in transgenic banana plants for development of sustainable resistance against Fusarium wilt

Although potent defensin molecules have been used for development of resistance against a host of fungal diseases in plants, they mostly function in a nonspecific manner at the fungal entry barrier level and hence are vulnerable to the evolution of resistance in the fungal pathogens against these defense molecules. Also, due to their broad spectrum non-specific mode of action several beneficial fungi, most importantly the arbuscular mycorrhizal fungi, are unnecessarily targeted by these defensin molecules affecting the normal growth and development of the host plants. To overcome these limitations, we investigated whether intron hairpin RNA (ihpRNA) (Wesley et al., 2001) mediated in plants expression of small interfering RNAs (siRNAs) targeted against important fungal genes (like velvet and fusarium transcription factor 1) in transgenic banana plants can lead to development of effective resistance against Foc in banana. Since this phenomenon works at the level of sequence homology between the siRNAs and the targeted fungal genes, no unintended off targets are expected to be affected by this strategy. Towards this goal, two fungal specific vital genes were selected and their partial sequences were assembled as ihpRNAs in plant binary vectors (Ghag et al., 2014). These binary vectors which were designed to express the two ihpRNA cassettes in constitutive fashion in transgenic banana plants were transformed into embryogenic cell suspensions of banana cv. Rasthali by Agrobacterium-mediated genetic transformation. Transformed banana lines which were confirmed to
express the fungal genes targeted siRNAs tolerated the 6 weeks long greenhouse Foc resistance bioassays without demonstrating any external and internal symptoms of Foc (Fig. 2). Presence of specific siRNAs expressed from the two ihpRNAs in transgenic banana plants was shown through Illumina sequencing of the total small RNAs isolated from the two groups of transgenic banana plants.

Banana Bunchy Top Disease (BBTD) of banana

Banana Bunchy Top Virus (BBTV) derives its name from the typical ‘bunchy top’ appearance shown by the infected banana plant. Under severe infection, the plant top gets choked with a rosette of narrow, short, erect and brittle leaves having yellow margins, which ultimately appear to be burnt. The infected leaves characteristically show dark green dots and dashes beside the minor leaf veins, which appear like hooks as they move into the edge of the midrib. Infected banana plants seldom produce a bunch and in case of late infections, a distorted bunch may be formed. BBTV is most commonly transmitted by banana aphid, Pentalonia nigronervosa and it can readily transmit through all different forms of vegetative planting material like suckers, corms and tissue culture plantlets (Hafner et al., 1995). Since no natural sources of resistance are known, use of planting material which is free from BBTV is the best way to control BBTD. Since the aphid vector is widespread and difficult to treat via systemic insecticides, a localized chance infection runs the risk of developing into a full-blown outbreak resulting in total loss of production. The severity of the disease coupled with complete lack of resistant cultivars necessitates the development of BBTV resistant banana cultivars through genetic engineering.

Host induced gene silencing (HIGS) of replication initiation protein gene of BBTV for development of sustainable resistance against BBTD

Using an approach similar to the one used to develop Fusarium wilt resistant banana plants, we explored the use of ihpRNA transcripts corresponding to viral master replication initiation protein (Rep) (Horser et al., 2001) to generate BBTV resistant transgenic banana plants. Two ihpRNA binary vector constructs namely ihpRNA-Rep and ihpRNA-ProRep were generated using Rep full coding sequence or Rep partial coding sequence along with its 5′ upstream region respectively and castor bean catalase intron. The Rep coding and 5′ upstream region were amplified from genomic DNA isolated from leaves of

Fig. 3: Transgenic BBTV resistant banana plants developed using HIGS strategy. (A) A BBTV infected banana plant. (B) Multiplication of banana aphid on in vitro banana plants. (C) Untransformed control banana plants showing characteristic BBTD symptoms 2 months after inoculation with viruliferous banana aphid. (D) Transgenic banana plants expressing the two ihpRNAs (targeted against replication initiation protein and its upstream regulatory region) show efficient resistance towards BBTV after a 2 months long bioassay with viruliferous banana aphid.
a BBTV infected banana plant. The two constructs were successfully transformed into banana embryogenic cells of banana cv Rasthali. ihpRNA-Rep and ihpRNA-ProRep derived transgenic banana plants were assayed for resistance towards BBTV infection using viruliferous aphids (Shekhawat et al., 2012). The transgenic banana plants generated using either of the constructs were completely resistant to BBTV infection as indicated by total absence of BBTD symptoms after 6 months of viruliferous aphid inoculation (Fig. 3). The resistance to BBTV infection in the two groups of transgenic plants was also proved by the fact that cDNAs coding for viral coat protein, movement protein and Rep protein could not be detected by RT-PCR in the inoculated transgenic leaves. Further, siRNAs specific to the sequence of Rep gene were detected in small RNAs isolated from transgenic leaves, establishing the basis of resistance of these plants towards BBTD.

**Conclusions and future directions**

The three strategies described above have successfully demonstrated the immense importance of the transgenic technology for development of improved banana varieties. Apart from disease resistance, we have also developed abiotic stress tolerance in transgenic bananas (Shekhawat et al., 2011) signifying the versatility of our approach (Fig. 4). Currently, our efforts are underway to develop transgenic bananas...
showing multiple disease resistance by stacking two or more of the transgenes in the same banana plant. These transgenic plants need to be tested in field trials after obtaining the necessary regulatory approvals.

References


Development of Indigenous Source of Cobalt Suitable for Radiation Technology Applications

Bhaskar Paul and A.K. Sharma
Materials Processing Division

and

M.F. Fonseca, R. Sadanandam and A.C. Bidaye
Former Colleagues at Materials Processing Division

and

K. Srikant
Metallic Fuels Division

Abstract

The present article highlights the developments made in the field of indigenization of the technology for preparation of cobalt shapes for radioisotope applications from a secondary resource. In the first step, the process of extraction of cobalt in the form of metal powder from a secondary indigenous resource as spent ammonia cracker catalyst is described. In the second step, the processes of conversion of cobalt metal powder into the desired shapes followed by coating over the finished products have been presented.

Introduction

The role of Cobalt-60 as a radiation source in teletherapy for the treatment of cancer needs hardly to be reiterated. Although not used commonly in developed countries, cobalt-60 teletherapy machines can still be regarded as a very viable and cost effective option for the treatment of a sizeable fraction of cancer patients. At present in India, there are only 399 teletherapy units (280 telecobalt units and 119 linacs). As per the IAEA advisory group criteria, it is estimated that more than 1000 teletherapy units will be required in the near future. Considering the large requirements of teletherapy, BARC has designed and developed an advanced telecobalt unit, which was named as Bhabhatron-II. While the success of Bhabhatron-II “lives” at the interface between many disciplines, its dependence on cobalt-60 source is arguably the strongest. The Board of Radiation and Isotope Technology (BRIT) fabricates and supplies 10 to 15 high intensity cobalt-60 sources to cancer hospitals annually for use in cobalt-60 teletherapy units. High specific activity (up to 320 Ci/g) 60Co pellets required for teletherapy is normally imported by BRIT.

BRIT has been supplying them, mostly using imported cobalt-60, while the development and launch of indigenous system Bhabhatron-II warrants further impetus to ensure sustainable indigenous sourcing of both high sp activity cobalt-60 and raw material for cobalt targets for irradiation.

60Co required for the fabrication of sources is produced in nuclear power reactors by the following nuclear reaction: 59Co (n,γ) 60Co. Cobalt metal (59Co) is loaded in adjustor rods in the form of nickel-plated cobalt pellets with the following dimensions: 1 mm diameter and 1 mm height. The activity induced depends on the duration of irradiation to the neutron flux in the reactor. The adjustor rods from the power reactors are then transported to the cobalt handling facility and then cut under water.

There are also other special NDT applications (e.g. in DAE Units; ISRO etc) requiring very high intensity Cobalt-60 (several hundred curie) for radiography (cf. conventional strength radiography cameras of Ir-192 and Co-60) and the sources for them need to be of very high specific activity comparable to that of sources for teletherapy. This requirement could also be met using the combination of indigenous raw material cobalt and irradiation in NPPs.
operating at high capacity factors. For these application nickel-plated cobalt pellets of 6 mm dia. x 25 mm height are activated in a nuclear reactor.

Among the main factors contributing to the activation of cobalt in reactor, the shape and size of cobalt pellets is important. The shape and size are important because irradiation time greatly depends on surface area of the material being exposed to radiation; smaller the material size, larger the surface area per unit mass and faster the irradiation. The important physical properties that are required for the pellets are its sintered density & dimensional accuracy. Sourcing cobalt raw material and manufacture of right size and shapes achieved by BARC adds greater strength to the indigenization efforts in a holistic manner.

India is one of the very few producers of large-scale industrial sources of cobalt-60 (typical sp acty 100 Ci/g; e.g. for industrial gamma plants) in the world. Thanks to our NPPs operating at high capacity factor over the past 4-5 years, the scope to produce cobalt-60 of much higher specific activity - upwards of 160-180 Ci/g, with potential to go above 200 Ci/g, and suitable for making teletherapy sources - gives India (BRIT, NPCIL, BARC) unique advantage to become self-reliant in the field of cobalt-60 in near future.

BRIT is in a position to access cobalt raw materials from direct import or through local agents. However, due to enforcement of technology control regimes, there is an uncertainty in their import. In addition, cobalt is a metal of strategic importance, neither primary resources of cobalt exist nor does indigenous large scale cobalt metal production exist. Therefore, all possible secondary resources of cobalt need to be explored to establish indigenous technology for the production of cobalt shapes for radio-isotope applications.

Materials Processing Division has investigated in detail some of these secondary resources like Alnico scrap, copper converter slag, beta cake from the zinc industry, deep sea nodules and spent ammonia cracker catalyst (SACC)\textsuperscript{1-4}. The last among these i.e, SACC, is interesting, since it is produced within DAE in large quantities as waste. The catalyst in the form of pellets is used to crack ammonia (for producing H2 in-situ). On long use, the catalyst pellets degrade, whereby they are no longer suitable for usage and are discarded. This discarded material can be procured from HWB (Thal, Maharashtra).

The Process

\textit{i) Extraction of cobalt from spent catalyst}

The entire process for extracting cobalt from the spent catalyst and its conversion to cobalt powder and finally to nickel plated shapes of the specified shapes is depicted in the flow-sheet Fig. 1.
The SACC catalyst pellets were analysed and the typical composition is reported (Fig 2). The as-received pellets dissolve easily in 2M H₂SO₄ at 60-80°C without any pretreatment/communion. A typical batch for processing these pellets involves 15 kg of catalyst pellets in 100 L Teflon lined stirred vessel. After leaching, Fe²⁺ is oxidized to Fe³⁺ with a slight excess (to stoichiometry) concentrated nitric acid. Subsequently, a suitable S/L separation is used before solvent extraction (SX).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Weight%</th>
</tr>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>36.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>31.5</td>
</tr>
<tr>
<td>CoO</td>
<td>29.5</td>
</tr>
<tr>
<td>NiO</td>
<td>0.27</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.70</td>
</tr>
<tr>
<td>Binder</td>
<td>1.53</td>
</tr>
</tbody>
</table>

SX using counter-current mixer-settlers is employed to separate Fe³⁺ and Al³⁺ from the oxidized leach liquor. The solvent used to achieve this consists of a mixture of 85% saponified 0.5M D2EHPA and 0.7M TBP in n-dodecane using 4 stages each for extraction and stripping. Stripping is carried out using 2M HCl. The raffinate is passed through an activated carbon column to make it free of any entrained/dissolved organic before ion exchange (IX).

SX raffinate, so obtained from the above treatment consists of essentially cobalt with a small nickel impurity. In order to remove this Ni, the solution (pH adjusted to -3.0) is passed through an ion exchange resin bed consisting of Dowex M4195 resin beads. Pre-conditioned resin partially fills the acrylic columns. Ni elution is facilitated with 0.25 M H₂SO₄, whereby the eluate is discarded after a suitable treatment.

The product solution obtained after ion exchange has a pH of -3.0 which is adjusted to 3.5 - 4.0 using 12.5M NaOH solution. A slight excess (over stoichiometry) of oxalic acid is added in order to precipitate cobalt as its oxalate salt. The pure solid is filtered using a nutsche filter which is then washed with sufficient quantity of DM water. Then it is dried at 110-120°C to constant weight to obtain the desired intermediate product, cobalt oxalate (Fig. 3), which is sent for further downstream processing.

ii) Conversion of cobalt oxalate to desired metallic shapes

Pure cobalt powder (Fig. 4) is obtained from thermal decomposition of cobalt oxalate at elevated temperatures under a reducing atmosphere of argon-4% hydrogen gas mixture in a specially designed decomposition reactor.
While the decomposition of cobalt oxalate begins at around 350°C as revealed by TG/DTA analysis (Fig. 5), the cobalt metal powder produced at this temperature is unstable and highly pyrophoric in nature and difficult to handle. The heating (and cooling) schedule of the oxalate has been optimized to yield cobalt powder with good flowability as well as sinterability. The SEM images of the cobalt oxalate and metal powder are shown in Fig. 6.

Good flowability and sinterability of the cobalt powder are needed because in the next step the powder is to be filled into silicone rubber moulds for making cobalt slugs or into a multi-cavity die having 100 holes of 1.2 mm dia. for making pellets. The rubber moulds are compacted at 250 MPa in a Cold Isostatic Press, while a bi-directional hydraulic press is used for compacting the powder to make pellets. The green compacts so obtained are sintered in a sintering furnace at 1300°C under reducing atmosphere. Process parameters like compaction pressure, sintering temperature and holding time for green cobalt pellets have been optimized for getting sintered density of more than 98% of theoretical density.

**iii.) Ni Plating over final shapes**

The radioactive cobalt slugs and pellets have to be shielded from the external environment and this is achieved by covering them with a layer of nickel. Two barrel plating facilities one for cobalt slugs with...
a barrel having 3 mm holes and another for cobalt pellets with a barrel having 0.8 mm holes have been commissioned and used for nickel coating of the cobalt slugs and pellets by the nickel electro-plating technique. The coating thickness is around 10 μm. The final products are displayed in Fig. 7.

**Conclusion:**

The process described here has enabled the extraction of a valuable metal from what is essentially a waste material and its subsequent conversion into shapes of both economic and strategic significance to the nation. It has permitted import substitution of a commodity whose procurement otherwise faced uncertainties due to export embargos. The entire technology was developed in-house and the entire plant and machinery is also indigenous.

**Acknowledgement**

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**References**

Isotope Techniques for Water Resources Management

Archana S. Deodhar, Md. Arzoo Ansari, Suman Sharma, Nobel Jacob, U. Saravana Kumar and Gursharan Singh

Isotope Hydrology Section, Isotope Applications and Radiopharmaceuticals Division

Abstract:
Isotopes in hydrology give a direct insight into the movement and distribution processes within the hydrological system. Water in its natural state contains environmental isotopes and conclusions may be drawn from their abundance variations. The isotopes commonly employed in hydrological investigations are the heavy stable isotopes of the water molecule, deuterium and oxygen-18 and the radioactive isotopes, tritium and carbon-14. The stable isotopes are excellent indicators of the circulation of water, while the radioactive isotopes are of special value in detecting the residence time, assuming no contamination of the water has occurred. The application of these techniques in connection with surface and groundwater in India are discussed briefly with four case studies. It can be concluded that these techniques complement the more traditional hydrological and hydrogeological methods employed in water resource investigations and that their use should be encouraged.

Introduction
The depletion in availability of water quantity and deteriorating water quality has posed a threat to the country, because these problems affect the lives of millions of people. The rapid growth of population coupled to steady increase in water requirements for agricultural and industrial development have imposed severe stress on the available freshwater resources in terms of both the quantity and quality, requiring consistent and careful management of water resources for their sustainable development.

For acquiring better quality of water, we need the continuation and extension of hydrological research. In this respect, the development and practical implementation of isotope methodologies in water resources management has proved to be very important. Isotope studies applied to a wide spectrum of hydrological problems, related to both surface and groundwater resources, as well as environmental studies in hydro-ecological systems are presently an established scientific discipline, often referred to as “Isotope Hydrology”.

Isotopes have wide applications in hydrological investigations and provide vital information for the better management of water resources. Isotopes (stable and radioactive) of both environmental as well reactor produced are routinely used as tracers in hydrology for various hydrological investigations (1) e.g., aquifer-aquifer interconnection, surface water-groundwater interrelation, source of groundwater salinity and pollution, origin of geothermal waters, efficacy of artificial recharge, dynamics in lakes, source of recharge & estimation of recharge to the groundwater etc.

A water molecule undergoes various natural phenomena in a hydrological cycle of which the two main physical processes responsible for the formation of precipitation are evaporation and condensation. When water from the ocean evaporates the lighter isotopes of hydrogen and oxygen go into vapor form preferentially while in condensation process the heavier isotopes will condense preferentially. Both these processes impart the variation of isotopic composition in the water molecules by fractionation of isotopes. The extent of such variation depends on various meteorological conditions, i.e. temperature, humidity, state of equilibrium of the process etc. In spite of several contributing factors, actual variation in isotopic composition in meteoric waters even at global scale is very small, which is measured using Isotope Ratio Mass Spectrometer (IRMS).

Isotopic concentrations are expressed as the difference between the measured ratios of the sample and the
reference over the measured ratio of the reference. The universally accepted way to report the isotopic compositions of natural water is deviations ($\delta$) and expressed in per mil (parts per thousand) from a reference standard mean ocean water (SMOW) as shown below:

$$\delta^{18}O = \left[ \frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{sample}} - \left(\frac{^{18}O}{^{16}O}\right)_{\text{SMOW}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{SMOW}}} \right] \times 10^3$$

The normal range of variations of $\delta D$ and $\delta^{18}O$ in nature are approximately – 450 to +100‰ and – 60 to +10‰ respectively and that the relative variation of $\delta D$ is about 8 times that of $\delta^{18}O$.

The commonly used isotopes for various applications in hydrology with their universally accepted standards are listed below in Tables 1, 2 and 3.

For the last four decades, scientists of Isotope Hydrology Laboratory, BARC Mumbai have successfully applied isotope techniques for investigating and solving problems related to water resources management in collaboration with a number of end user organisations including state and central water authorities. Some of the recently carried out isotope hydrological investigations are presented here.
A. Source and Mechanism of Groundwater Recharge:

1. Isotope hydrological investigation for recharging of the drying springs in mountainous regions of Uttarakhand and Himachal Pradesh

In the mountainous regions, springs are the only available source of water for drinking, irrigation and other uses but their low discharges during summer cause a lot of hardship to the people. To enhance discharge and duration of the springs by artificial recharge methods, an isotope hydrological investigation was carried out at 4 locations in Uttarakhand (Brahmkhal, Pipaya, Kakodakhal and Isala) and at 2 locations in Himachal Pradesh (Surla and Dhauli/Kandela), in collaboration with Himalayan Environmental Studies and Conservation Organisation (HESCO), Dehradun.

Environmental isotopes ($^{18}$O/$^{16}$O, $^3$H/$^1$H, $^1$H) along with hydrogeochemistry and geomorphology was employed to identify the recharge zones of the drying springs. Isotopic composition of isotopes in water is affected by several factors like temperature, season, latitude, altitude, distance from the coast and amount of precipitation. Orographic precipitation caused by rise of vapor mass over landscape in mountainous region results in variation of isotopic composition owing to difference of altitude at various locations. Therefore, at higher altitudes, where average temperatures are lower, precipitation is isotopically depleted compare to the lower altitude. This is commonly known as 'altitude effect' and this is used to locate recharge area at project sites.

The $^8$O versus discharge elevation of the springs at Surla (Fig.1) gave an altitude effect (rate of change of isotopic composition of precipitation with respect to
altitude) of –0.23‰ per 100 m elevation (3). Based on the obtained altitude effect and using \( \delta^{18}O \) of a rainwater samples collected, a relationship between \( \delta^{18}O \) of rainfall versus elevation was obtained:

\[
\delta^{18}O(\text{‰}) = -0.003(\text{‰}/\text{m}) \times \text{elevation (m)} - 5.1(\text{‰})
\]

(Fig. 2). The recharge elevations in the valley range from +700 m amsl to +1150 m amsl.

Similarly from the stable isotope data of rainwater, altitude effect was estimated for each location and recharge zones of the drying springs (47 Nos.) were identified. At the identified recharge areas suitable rain water harvesting structures like contour-bunding, or building of check dams or levees structures were constructed.

The measurement of discharge rate of springs after the construction of rain water harvesting structures showed an increase in spring discharge at all the sites and they have not dried up in the advent of summer. There is an increase in discharge up to 72% in Surla site, Himachal Pradesh, although there is a significant decrease in rainfall of 22% in 2013. Similarly, an increase in discharge ranging between 21 to 145% is observed at Kakodakhal site, Uttarakhand.

2. Environmental isotope investigation on groundwater recharge from irrigation tanks at Tirumal Village, Madurai, Tamil Nadu

Madurai district is a water scarce, semi-arid region in southern part of Peninsular India. Currently, tank-fed agriculture development programme is being implemented in this region by utilizing the large number of traditionally existing minor irrigation tanks. These irrigation tanks are being renovated and developed for water conservation in order to facilitate groundwater recharge and water usage during non-monsoon months.
An isotope hydrological investigation was conducted at Tirumal Village, Madurai, in collaboration with DHAN (Development of Humane Action) Foundation, to demarcate the area of influence of recently renovated Urappareddy cascade of irrigation tanks (4 tanks) and thereby quantify the their contribution to the groundwater recharge. Pre & post monsoon samples were collected from the irrigation tanks, open wells upstream and downstream of the tanks, bore wells etc. (Fig.3) and analysed for $\delta^2$H, $\delta^{18}$O, $^{222}$Rn and hydrochemistry. Field parameters such as temperature, electrical conductivity, pH, alkalinity, DO and groundwater levels were measured in situ. Hydro chemical results indicate that the wells away from the irrigation tanks are brackish in nature. Also, most of the well samples show nitrate pollution probably because of the excess use of fertilizers in this area.

The down side well samples lie in a mixing line between the tank water and the rainwater in the $\delta^{18}$O- $\delta^2$H plot (Fig. 4), indicating groundwater recharge from the irrigation tanks. Higher $^{222}$Rn activities and lower electrical conductivities are observed in the post monsoon samples, indicating groundwater recharge through the weathered zone. The recharged plumes downstream of the tanks were demarcated and the longitudinal spreads of the plumes were found to vary from 0.5 km in the uppermost tank to 1 km in the lowermost tank. It is found that the renovated tanks are effective in recharging the groundwater in these water scarce regions.

B. Geothermal Studies:

1. **Isotope hydrological investigation on geothermal springs at Tural and Rajwadi areas, Chiplun, Ratnagiri, Maharashtra**

Geothermal sources are one of the important alternative energy resources for any country. In India, there are a few hundred such sources available but because of their low surface temperatures, they are not yet exploited for power generation. There are about 18 such geothermal prospects located along the west coast of Maharashtra.
For the first time in the country, Maharashtra Energy Development Agency (MEDA) has taken up the development and exploitation of these geothermal sources for power generation and the project has been awarded to M/s. Thermax Ltd, Pune. At the request of M/s. Thermax, isotope hydrology investigations are underway at two geothermal sites, namely Tural and Rajwadi, near Chiplun in the Ratnagiri district with objectives to understand the source and mechanism of recharge and to estimate the subsurface reservoir temperatures of the hot springs.

Hydrogeochemistry, ratios of environmental stable isotopes (\(^{18}O/^{16}O\), \(^{2}H/^{1}H\), \(^{3}H\), and \(^{222}\)Rn content present in waters of hot springs and other nonthermal sources were determined on pre-monsoon water samples. The \(^{3}H-^{18}O\) plot (Fig. 5) of the water samples indicated considerable \(^{18}O\)-shift along \(^{18}O\) axis for hot springs. This higher \(^{18}O\) content in ambient water is generated due to rock-water interaction which is usually possible at temperature greater than 150°C only. The results also indicate that the hot springs waters are meteoric in origin and fed by earlier year’s rain waters. The chemistry of the hot waters as suggested by the piper plot (Fig.6) are Na-Cl type, hence are mature waters for the power exploration. The chemical geothermometry based on dissolved cations and silica also estimated reservoir temperature \(\sim\)140-160°C. The heat source is, probably, from deep buried magma (mantle) and not from the radiogenic reactions occurring in the granite as inferred by the low \(^{222}\)Rn content of the waters, which forms the basement for the Deccan Basalt at a depth of about 1000 m. The investigation suggests that, these geothermal resources are potential for electricity generation.

C. Groundwater pollution studies:

1. **Isotope hydrochemical investigations on pollution of groundwater by fly ash dumped in coal open cast mines at Talcher thermal Power Station of NTPC, Odisha**

Safe disposal of fly ash generated by coal based thermal power plants is a major issue for the power plant management as well as the environmentalists as it contains several toxic chemical constituents which may pollute the environment.

Talcher Thermal Power Station of NTPC generates 10.1 Million CUM of fly ash per annum. The Talcher Coalfields located near the power station have three large abandoned coal mines. The back filling of voids with fly ash could resolve the twin issues i.e. disposal of fly ash and saving of NTPC revenue. The fly ash is mixed with fresh water in the ratio of about 2:8 to make slurry and pumped into the quarries using large pipes. The River Brahmani flowing close by, provided fresh water which is being pumped into the power station for making the slurry.
The Technical Appraisal Committee of the Ministry of Environment asked the NTPC management to take the help of BARC, Mumbai, to study the groundwater pollution, if any, before continuing with the disposal. Isotope hydrology investigations have been initiated to understand whether the chemical constituents in fly ash leachate are polluting groundwater in downstream area or not. Water samples from mine, groundwater, surface water and rain water were analysed from the study area (Fig.7) for environmental stable isotopes ($\delta^2$H, $\delta^{18}$O), Tritium, trace elements and major cation and anion. Parameters like EC, pH were measured insitu. Isotope data suggest that, the hand pumps are getting recharge from both rain water and the mine water. Tritium values of a few hand pump samples are 2 – 4 TU and local rain water is 4 TU. Hence some wells are mixture of both modern water (shallow aquifer) and older water (deep aquifer). Isotopic data suggest that groundwater in the southern and S-SE part of area near the quarry is influenced by quarry water (Fig.8). The drainage pattern of the area also substantiates this finding. A bore well (14A), which is nearby an old abandoned fly ash pond, measured comparably higher concentrations of Mn and Zn which is above maximum permissible limit (MPL) of drinking water, may be getting recharge from the old abandoned fly ash pond along with rain water. The fly ash leachates in these mines are getting well-diluted due to continuous fresh water input from River Brahmini, and hence don’t pose any threat to groundwater in downstream. Periodical (annual) chemical analysis of groundwater samples are to be carried out to ensure that the chemical toxicity don’t exceed MPL for drinking water. To bring down the higher concentrations of toxic ions in well No 14A the old abandoned fly ash pond needs to be fed with continuous supply of fresh water.

The above discussed case studies clearly indicate that Isotope techniques have proved to be effective tools for solving many critical hydrological problems and in many cases, provide information that could not be obtained by any other means. With advent of simple to operate instruments for measurement of various isotopes like liquid isotope water analyser etc, the application of isotope hydrology techniques for water resources development and management is expected to multiply enormously in India and abroad in the coming years.

References:
Bhabha Atomic Research Centre celebrated National Science Day-2014 with Chemfest-2014, a festival of Chemistry. The primary aim of the festival was to showcase the achievements of chemists of BARC in fields such as Nuclear Energy, Hydrogen and Solar energy, Health, Environment, Industrial & Societal Applications. The festival consisted of posters, exhibits, short lectures on topics of current interest, film shows covering achievements of DAE and interactive sessions with senior scientists. The venue was Training School Hostel & Guest House and Homi Bhabha National Institute, Anushaktinagar. The festival was open to public for four days; February 28- March 03, 2014. During these days, on the display were over 160 posters, 30 exhibits, 20 films, 16 lectures of 30 minutes each and four interaction sessions with senior scientists. The fest had a good mix of other disciplines namely, Physics, Electronic and Instrumentation, and Health Physics. A team of over 150 volunteers managed the festival in a professional manner. A large number of University and college students and faculty were invited to participate.

The festival was inaugurated on National Science Day, February 28, by Dr. R.B. Grover, Director, HBNI, Dr. J.V. Yakhmi, Chairman, AEES and Dr. R.M. Iyer, former Director, Chemistry Group, BARC.

During four days, over 1000 students accompanied by over 100 teachers from 21 colleges in and around Mumbai and nearby places attended the festival. The colleges include R. Jhunjhunwala College (Ghatkopar), V.G. Vaze College (Mulund), Modern College (Vashi), Sandesh College (Vikhroli), SIES College (Sion), Sri Sri Ravishankara School (Dharavi), Dept. of Chemistry, Mumbai University (Kalina), Vivekanand College (Chembur), Konkan Gyanpeeth College (Karjat), Birla College (Kalyan), Institute of Science (Fort), SNDT University (Juhu), Somaiya College (Vidyavihar), ICLE’s Motilal Jhunjhunwala College (Vashi), Deolali High School (Nashik), St. Joseph School (Panvel), A.E.C.S School-1, 2,3,4 and 5 (Anushaktinagar). In addition, a large number of BARC/NPCIL/HWB employees visited Chemfest-2014 along with their family members. All four days of the festival experienced an overflowing enthusiasm and interest from the students, teachers and other visitors.

The display and posters in the Chemfest were organized in five thematic sections: (1) Energy including chemistry in front and back end of nuclear fuel cycle, hydrogen energy and solar energy, (2) Societal applications including clean water, fluoride/arsenic remediation, (3) Chemistry for Environment, (4) Chemistry for Health and (5) Chemistry at fundamental level. Some of the innovations ready for technology transfer were also displayed in the Chemfest. The students were also advised on the carrier prospects in basic sciences and also on how to join R&D in BARC.

Chemfest provided a unique opportunity to college and university students to know about the current research in BARC, to listen to topics of their interest and to interact directly with scientists/engineers. The interactive session with senior scientist, i.e., with Prof. J.B. Joshi, Homi Bhabha Chair Professor (on February 28, FN), Dr. V.C. Sahni, Homi Bhabha Chair Professor (on February 28, AN), Dr. Sekhar Basu, Director BARC (on March 01, AN) and Dr. J.P. Mittal, M.N. Saha Professor (on March 03, AN) were enjoyed by one and all.

Several students and teachers suggested that such programmes be organized by BARC in regular intervals and that will benefit the students in a continual manner.
The Indian Association for Radiation Protection organised its 31st National Conference (IARPNC-2014) on the “Advances in Radiation Measurement Systems and Techniques” at Multipurpose Hall, BARC Training School Hostel, Anushaktinagar, Mumbai during March 19-21, 2014. The conference was attended by about 400 scientist, including Radiation Protection professionals from DAE, IAEA, DRDO, industry. Invited speakers both from India and abroad shared their expertise and important insights in the field of radiation protection. One of the important features of the conference was the participation of a large number of students and professors from universities from all over India.

The scientific deliberations of the conference included latest systems and techniques developed for radiation measurements, environmental radioactivity, assessment of radiation exposure to the public from natural radiation and emergency preparedness. There were thirteen invited talks; notable amongst them were the ones on Fukushima accident by Dr. T. Suzuki, an IAEA expert from Japan, Epidemiological investigations by Dr.K.B.Sainis, Former Director, BMG and Dr R.A.Badwe, Director, Tata Memorial Centre, Mumbai. Dr. Sainis noted that comprehensive data from high background radiation areas of Kerala from a cohort of more than 300,000 persons exposed to high levels of natural radiation did not show any incidence of excess cancer rates over the incidence rates in normal population. These studies lead to non-applicability of linear no threshold (LNT) model at least for doses below 100 mSv. Dr. Badwe informed that the cancer incidence rates are about 40 for 100,000 persons in rural area and about twice of this in the urban areas. The extensive studies undertaken by TMC, have also not indicated any additional cancer incidences, attributable to power plant operations in different regions in India as compared to those observed in nearest control population.

There was a lively panel discussion on ‘Nuclear Power, Radiation Protection and Public Perception’ on the concluding day of the conference. The panellists included experts from BARC, AERB, NPCIL and DAE. Many panellists expressed their views that based upon the international research, there may be a possibility of having a threshold dose below which there is no risk for exposure to external radiation or can have benefits as predicted by the radiation hormesis.

Dignitaries (from L to R) : Dr. K.S. Pradeepkumar (Head, RSSD, BARC), Shri S.S. Bajaj (Chairman, AERB), Shri B.Bhattacharjee (Hon. Member, NDMA, New Delhi), Dr. D.N. Sharma (Director, HS&EG) and Dr. M.S. Kulkarni (Convener, IARPNC-2014)
During the period between December 2013 and February 2014, BARC has transferred seven technologies to various industries. Technology Transfer & Collaboration Division (TT&CD) co-ordinated these technology transfers. The details are given below:

A. BARC through its Centre for Incubation of Technologies has signed the MoU with following parties.

1. M/s Utopia Automation & Control Pvt. Ltd., Satara, (Maharashtra) for “Development of nano particles of Lithium Titanate (Li4Ti5O12) and core shell nano particles of Lithium Iron Phosphate (LiFePO4) coated with Graphene manufacturing process” technology on December 02, 2013

In this incubation nano particles of Lithium Titanate (Li4Ti5O12) and core shell nano particles of Lithium Iron Phosphate (LiFePO4) coated with Graphene manufacturing process will be developed from the lab scale knowledge at BARC to a ready-to-market level product at BARCIT.


A nutraceutical formulation based on turmeric extract in which curcumin is the active principle. The product would be used as dietary supplement in the form of a drink. The turmeric extract would be a component of the drink in addition to the necessary nutrients like milk proteins, vitamins, sugar and carbohydrates. Due to the presence of milk proteins, the curcumin will not degrade and can get released in blood for quick circulation. The amount of turmeric extract will be expressed in terms of curcumin content. In this incubation Nutraceuticals will be developed from the lab scale knowledge at BARC to a ready-to-market level product at BARCIT.

B. Nisargruna Biogas Technology based on biodegradable waste has been developed by NA&BTD. The plant processes biodegradable waste into biogas and weed free manure. The technology has been transferred to 103 parties already and more than 150 plants are operational in the country. It was further transferred to the following four parties-

- M/s 3S Envo Solutions, Mumbai on 30.1.2014

C. Technologies of “TLD Phosphor and TLD Badge” developed by Chemistry Division and Radiological Physics & Advisory Division (RP&AD) respectively have been transferred to M/s. Adithisri Radiation Services, Tirupati on 10.1.2014

TLD Phosphor:

Of the thermoluminescence phosphors, dysprosium doped calcium sulphate (CaSO4:Dy) phosphor is one of the most efficient phosphors for use in
radiation dosimetry, i.e. for monitoring the radiation (Gamma or X-ray) dose received by personnel working with radiation. Briefly the process consists in dissolving requisite amounts of both the high purity calcium sulphate and dysprosium oxide (Dy2O3) in conc. Sulphuric acid (H2SO4) and then crystallizing out the product by distilling off the H2SO4 under reduced pressure. The crystallized product is annealed at a desired temperature or quenched to achieve the high sensitivity of the phosphor powder. This phosphor powder is the raw material for making TLD Badges.

phosphor is blended with Teflon powder for making TLD disc dosimeter. TLD badge consists of three nos. of disc-dosimeters that are clipped on to the holes made on a metallic card, which in turn is housed into a plastic cassette. The first disc has Al and Cu combination filter, the second disc has a plastic filter and the third disc has no filter. The metal filters on the first disc cut-off the beta radiation and the disc gives TL due to X & gamma radiation. The plastic filter on the second disc cuts off soft-beta radiation and records X, gamma and hard beta radiation, where as the third disc (with no filter) records all the radiation. Algorithms involving these filter combinations of 3 disc-dosimeters help in identification of the types of radiation (X, gamma and beta) to which the badge is exposed and estimation of whole body and skin dose. The TLD Badge is used by the occupational radiation workers in the nuclear fuel cycle, medical, industrial and research applications of radiation. It can measure doses ranging from 100 µSv to 10 Sv.

TLD Badge:

Thermo Luminescence Dosimeter (TLD) badge is a device worn at the chest level by the radiation worker for monitoring the ionizing radiation he is exposed to. It is based on the phenomenon of thermo-luminescence i.e. emission of light from certain materials when heated after being exposed to radiation. The emitted light intensity is measured with Photo Multiplier Tube. Proportionality between the radiation exposure and thermoluminescence yields to radiation dose measurements. The raw material of the badge is dysprosium doped CaSO4 TLD phosphor. This
Responsibility (CSR) application of Eastern Coalfields Limited (ECL), West Bengal a Subsidiary of Coal India Limited (C.I.L)

- Nisargruna - Biogas plant based on biodegradable waste
- Soil Organic Carbon Detection & Testing Kit
- Vibro Thermal Disinfester
- Foldable Solar Dryer (FSD)
- Process for retaining pericarp colour and extending shelf life of Litchi
- Solar Energy Driven Portable Domestic Brackish Water Reverse Osmosis (BWRO) technology
- Domestic Water Purifier (DWP)
- Dip N Drink Membrane Pouch

E. BARC transfers know-how of “A rapid, continuous and renewable method for production of the anti-cancer drug Camptothecin” to Patanjali Bio Research Institute (PBRI), Haridwar on Feb 5, 2014.

This technology has been developed by Nuclear Agriculture & Biotechnology Division (NA&BTD). It is a Plant tissue culture method for the continuous and enhanced production of the anticancer quinoline alkaloid camptothecin using multiple shoot cultures of Ophiorrhiza rugosa var decumbens. The yield of camptothecin in the cultures is found to be 0.056 % dry weight during a period of 35 days and the parent plant contained 0.002 % dry weight.
The DAE-BRNS conference on “Organic Devices: The Future Ahead (ODeFA-2014)” was held at Training School Hostel, BARC, Anushaktinagar Mumbai during March 3-6, 2014, which was organized by Technical Physics Division. The main objective of this conference was to discuss on the current status, challenges and new developments as well as frontier applications of organic materials based devices, such as, solar cells, flexible electronics, sensors, radiation detectors, energy storage etc. The topics covered in the conference are: (i) Synthesis of novel materials for organic devices (ii) Role of organic films and interfaces in organic devices (iii) Charge transport and photoresponse (iv) Flexible organic photovoltaic’s (v) Organic memories and detectors (vi) Characterization techniques for organic materials.

In the inauguration function, Dr. D.K. Aswal, Convener ODeFA-2014, welcomed the delegates and explained that organic devices have a good future because of their lost cost manufacturing and mechanical flexibility. He mentioned that for the conference there are 3 Plenary Lectures from renowned scientist of international repute, 21 Invited Talks, and 110 contributed presentations. Dr. K. L. Ramakumar, Director Radiochemistry & Isotope group, in his speech as a Chief Guest suggested the importance of organic materials for next generation devices and their implication for DAE related activity. Dr. S. L. Chaplot, Director Physics Group, in his presidential address mentioned the importance of DAE facilities such as Synchrotron source and neutron scattering for the characterization of organic materials. Dr. S. K. Gupta, Head Technical Physics Division, in his key note address discussed the future of flexible organic devices such as solar cells, field effect transistors and displays over the conventional silicon based technology. Dr. Ajay Singh, Secretary ODeFA-2014, presented a vote of thank
a overview of new synthesis techniques of organic materials for photovoltaics, and in the another Plenary Lecture delivered by Prof. Anders Hagfeldt, Uppsala Univ., Sweden, discussed the latest development in nanostructured solar cells and demonstrated the fabrication of solar cells with 16% efficiency. Prof. A. Mishra, University of Ulm, Germany discussed functional S,N-heteroacene-based oligothiophenes for solar cell applications. Prof. Mohamed Jouini, University Paris Diderot France discussed on the low-cost and environmentally-friendly method to produce conducting polymers as hole carriers in photovoltaic devices, and Dr. H. N. Ghosh, BARC, Mumbai delivered a talk on ultrafast charge transfer dynamics supersensitized quantum dot solar cells.

The topic Organic memories & detectors was covered by three speakers. Prof. Deepak, IIT-Kanpur discussed on ferroelectric organic memories, while Dr. S.P. Koiry, BARC, Mumbai explained the concept, design and synthesis of organic memory materials. Prof. Beatrice Fraboni, Università di Bologna, Italy explained the ionizing radiation sensors based on semiconducting organic single crystals.

Under the topic, Characterization techniques, Prof. K. Marumoto, University of Tsukuba, Japan, explained the development of new analytical methods for microscopic characterization of organic devices with electron spin resonance, and Dr. V.K. Aswal, BARC-Mumbai, discussed the small angle neutron scattering for structure and interaction determination in amphiphilic systems.

In the concluding session, four researchers which were selected for the innovative research award delivered their oral presentations. Dr. D. K. Aswal made summary of the symposium, suggesting that organic devices has a bright future and the scientist and engineers should come close to achieve the goal.
Barc Scientist Honoured

Padma Shri Award for Shri Sekhar Basu, Director, BARC

Shri Sekhar Basu is a renowned nuclear scientist. He worked as Project Director of the Nuclear Submarine Programme and as Chief Executive of the Nuclear Recycle Board at BARC, before taking over as Director, BARC in 2012. Shri Basu is an Engineer of exceptional ability who has played a lead role in multiple areas of nuclear science and engineering and is a major contributor in establishing India as a leader in nuclear field.

Shri Basu was born on 20th September 1952 and did his schooling from Ballygunge Government School, Kolkata. Later he graduated in Mechanical Engineering from Veermata Jijabai Technological Institute (VJTI), University of Mumbai in 1974. After completion of the one year BARC Training School programme in nuclear science and engineering, he joined the Reactor Engineering Division in 1975. He started his career by designing fuel for Boiling Water Reactor, which showed excellent performance. Later he took up the responsibility for the development of the nuclear submarine propulsion plant and built the land-based prototype at Kalpakkam from scratch. He continues to guide the Indian nuclear propulsion programme for the sea going versions. Since 2000, he is also responsible for the design, development, construction and operation of nuclear recycle plants at Tarapur and Kalpakkam. These plants are performing to international standards. Shri Basu is pursuing the design of the Integrated Nuclear Recycle Plant, which will take the nuclear waste management programme to a greater height.

As Chairman of the Project Management Board, he is responsible for the development of the Indian Neutrino Observatory at Tamil Nadu and as Apex Project Co-ordinator, he is spearheading the development of the 1 Gev Superconducting Accelerator for the Accelerator Driven System Programme. Shri Basu is also guiding the establishment of a nuclear fuel cycle park involving research reactors and fuel fabrication & reprocessing facilities at the BARC Vizag campus. Work on the design of Indian Pressurised Water Reactor has also been initiated by him.

As Director, BARC, Shri Basu has taken special initiatives for major expansion in the societal programmes of DAE in the areas of nuclear agriculture, food preservation and nuclear medicine. While pursuing basic research in the field of nuclear science and engineering, he is also working towards the expansion of enrichment and strategic programmes. He represented India in concluding ‘Arrangements and Procedures’ with the US Government for reprocessing of US hypothecated fuel and has chaired the International Committee for the design review of some modules for the International Thermonuclear Experimental Reactor (ITER) programme.

Shri Basu has several publications to his credit in national and international journals. He has been conferred the Indian Nuclear Society Award 2002 and DAE Awards in 2006 and 2007. He is a Fellow of the Indian National Academy of Engineers (INAE) and the Indian Society for Non Destructive Testing (ISNT). Jadavpur University, Kolkata awarded him the DLit (Honoris Causa) degree in 2013. He was awarded Padma Shri by the Government of India and this award was conferred on him by the President of India at Rashtrapathi Bhavan, New Delhi, on 31st March 2014.
Padma Shri Award for Dr. R.B. Grover, Director, HBNI

Dr. Ravi Bhushan Grover is Director, Homi Bhabha National Institute and occupies Homi Bhabha Chair instituted by the Department of Atomic Energy (DAE). He is a Member of the Atomic Energy Commission, the Board of Research in Nuclear Sciences and the DAE Research Council. He has been the sous-Sherpa of the Government of India for the Nuclear Security Summit process since 2009. He has been leading India’s delegation to ITER Council since its inception. He is a Fellow of the Indian National Academy of Engineering (INAE) and also of the World Academy of Art and Science.

Born on 17th Feb., 1949, Dr. Grover studied mechanical engineering at Delhi School of Engineering, Delhi University and nuclear engineering at BARC Training School. He joined Bhabha Atomic Research Centre (BARC) in 1971 and up to 1996 worked as a nuclear engineer specializing in reactor thermal hydraulics. In parallel, in 1982, he received a PhD in the faculty of engineering at Indian Institute of Science, Bangalore. Post 1996, he worked in various capacities in BARC including as Head of the newly established Technology Transfer & Collaboration Division; and Director, Knowledge Management Group. He was Head of the Strategic Planning Group, DAE since its setting up in December 2000 until his superannuation on 28th February 2013. He was Principal Adviser, DAE (in the rank of Secretary to Government of India) from October, 2010 to February 2013. He was involved in conceptualizing the setting up of HBNI, a deemed to be university under the Department of Atomic Energy and was nominated its Founder Director in June 2005.

Dr. Grover was responsible for core and fuel thermal hydraulics, and safety analysis of the research reactor-Dhruva- a first such job in India. He did similar work also process design of systems and equipment for a compact light water reactor. In 2004, Dr. Grover completed formulation of a scenario for growth of electricity demand for the next five decades, first such long-term forecast in India.

Besides distinguishing himself as an engineer, Dr. Grover played a maximum role in all steps taken by the Government of India towards opening international civil nuclear trade. This involved negotiations with professionals from many advanced countries and International Atomic Energy Agency. He was part of the team involved in outreach with member-countries of the Nuclear Suppliers Group (NSG) which led to NSG amending its guidelines facilitating international civil nuclear trade with India.

Dr. Grover was bestowed with Lifetime Achievement Award of the DAE on 15 January 2013. Other awards won by him include Distinguished Alumnus Award by Indian Institute of Science and Indian Institute of Science Alumni Association in 2011; Distinguished Alumnus Award by Delhi College of Engineering Alumni Association in 2009; Dhirubhai Ambani Oration Award by Indian Institute of Chemical Engineers in 2008; and Indian Nuclear Society Award-2006 for Nuclear Reactor Technology, including Nuclear Safety. He was President of the Indian Society of Heat and Mass Transfer for the period 2010-2013. During a career spanning four decades, Dr. Grover has distinguished himself as an academic, research and development engineer, a science administrator and a nuclear diplomat.
Exceptional Service Award

Dr. V.V. Kulkarni, Project Director (New Technologies), BARC, was honoured with the Exceptional Service Award by the Prime Minister of India on 24th April, 2014.

His citation reads, “On behalf of the Prime Minister of India, I commend Dr. V.V. Kulkarni, Project Director (New Technologies), BARC for his exceptional service to the nation. Over the last five decades, Dr. Kulkarni has worked with exemplary commitment, resolve and a sense of duty, often at considerable personal sacrifice, in one of the most complex and challenging areas of Science and Technology. Through his excellence in scientific research, project management and systems development, he has played a vital role in a national mission of critical importance.

The nation is proud of Dr. Kulkarni’s enormous and unique achievements and expresses its deepest gratitude for his lifelong service”.

Name of the Scientist : Dr. S.M. Yusuf, SSPD
Name of the Award : P.K. IYENGAR MEMORIAL AWARD for excellence in Experimental Physics (2012)
Instituted by : Indian Physics Association, The award was present on 11th April 2014.
Name of the Scientists : Sudhir Kumar, D. Datta*, S.D. Sharma, G. Chourasiya and D. A. R. Babu
Affiliation : Radiological Physics & Advisory Division, *Health Physics Division, BARC
Name of Award : Best oral paper award of Association of Medical Physicists of India
Title of the Paper : “Estimation of distance error by fuzzy set theory required for strength determination of HDR 192Ir brachytherapy sources”
Presented at : 34th National Conference of Association of Medical Physicist of India (AMPI) held at Saha Institute of Nuclear Physics (SINP), Kolkata during November 13-16, 2013.
Cirus & Dhruva Research Reactors at BARC