

Editorial

Keeping pace with the current developments and continuous updating, in addition to implementing the original ideas form the basis for quality research. Our founder H.J. Bhabha realized the importance of research and said, "No country which wishes to play a leading part in the world can afford to neglect pure or long term research". In the modern era of multi-disciplinary approach to a research problem, be it basic sciences or applied sciences or technological developments, team effort and collaborations are important. University research, both basic and applied, can be a catalyst to scientific and technological advances. In the developing countries like ours, sustenance of quality research in the universities often suffers from the paucity of funds. By sponsoring joint research, it is possible to not only tap into the knowledge of our academia and students, but also harness the efficiency and cost effectiveness of carrying out research in a university. Such collaborations help evolving a mechanism for closer interaction with the problems of mutual interest to institutions like various units of Department of Atomic Energy on one hand and the universities and research institutions, on the other hand. Board of Research in Nuclear Sciences (BRNS) under the Department of Atomic Energy (DAE) has been instrumental in establishing fruitful partnerships and linkage between educational institutes and research institutes. BRNS attaches importance to promote research in academic / research institutes in the country in the areas of interest to the department.

It was thought to bring out an issue on BRNS interaction with research institutes with a view to providing some glimpses on the work that is being carried out with BRNS funding. IANCAS is fortunate that Dr. R.B. Grover accepted to be the Guest Editor for this issue and I thank him for the apt selection of the topics and experts as authors. There are 10 articles in this issue and all are interesting and informative. Dr. Grover explains the details of the mechanism of selecting, supporting and monitoring a project in his article on Alliances for R&D. BRNS initiated a coordinated research project to investigate

(Contd.).

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thermal ecology around the nuclear power plants in South India and Dr. S.K. Apte described aims, objectives and the progress made so far, in his article. Prof. B.S.M. Rao describes about the forthcoming National Centre for Free Radical Research in the campus of University of Pune, Pune. I thank all the authors for timely contribution of the articles. I am grateful to Dr. J.P. Mittal, Dr. D.D. Bhawalkar, Dr. S. Banerjee and Dr. N. Ramamoorthy, Chairmen of the four advisory committees of BRNS for giving Focus articles to this issue.

The highlight of this issue is a stimulating interview with Shri B. Bhattacharjee, Director, BARC in which Director gave his views and ideas on the various R&D work in BARC and collaborations with the Universities and research institutions. On behalf of members of IANCAS, I record our gratitude to Shri B. Bhattacharjee for sparing his valuable time for the interview and encouraging the activities of IANCAS.

I take this opportunity to wish one and all "a very happy, prosperous and scientifically satisfying new year 2003".

A.V.R. Reddy

Stable Environmental Isotope Variation 55 in the Karstic Terrain and Delineation of Groundwater Recharge Area in the Western Part of Chhattisgarh Basin, India

*Ninad Bodhankar, K.M. Kulkarni,
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U.P. Kulkarni*

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S.R. Pujari*

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Shreekumar Apte



President's Message

The Department of Atomic Energy has defined its mandate in the form of six key drivers and one of them is "Research Education Linkage". This has been expanded as, "mutual strengthening of educational and research in nuclear and allied sciences, and technologies". All units of DAE have given due importance to this and BARC being the premier institute has been contributing significantly towards this over the last five decades. This activity encompasses both basic sciences and technologies. In view of large activities involved, it was felt that IANCAS bulletin on this topic will be very useful to the readers.

In the last thirty years the knowledge-base is expanding at a very fast rate and even with modern communication systems, it may be difficult for many to update in one's own and allied fields. It is in this context a constant interaction between institutes like BARC and Universities is a must. We all have realized the importance of collaborative work and already have different bodies like BRNS and IUCDAEF for its implementation. The important feature of this bulletin is nine articles on BRNS projects which are of interest to IANCAS members. This bulletin will not only serve as the guideline for those who are not yet part of this chain, but also help in taking the stock of the existing setup for future improvement. Shri B. Bhattacharjee, Director, Bhabha Atomic Research Centre supported this proposal and guided us so as to make this bulletin attractive and useful. He also gave an interview in which he expressed his views with focus on the theme of this bulletin. On behalf of IANCAS I thank him for the same. Senior scientists of DAE, Dr. J.P. Mittal, Dr. D.D. Bhavalkar, Dr. N. Ramamoorthy and Dr. S. Banerjee, Chair persons of different BRNS committees have given their views, which enhanced the quality of the bulletin. I will like to thank Dr. R.B. Grover for agreeing to be the guest editor and Dr. Reddy for their hard work in bringing out this excellent bulletin.

On behalf of IANCAS and my personal behalf I wish all of you a happy and prosperous new year 2003.

S.B. Manohar

From the Secretary's Desk



Dear Members,

Greetings to you all for a happy and prosperous new year, 2003.

A key element of advancing the capabilities and to foster a vibrant and dynamic research infrastructure in the relevant areas is collaboration between the Academia and National laboratories. It is imperative that this cooperation is extended now to maximize opportunities ensuing from several recent developments. With this view, BRNS plays a pivotal role in encouraging researchers from universities and research institutes with wide-ranging funding, under various schemes, to enter in to collaborative research programmes with DAE facilities. Such an alliance would facilitate access to specialized and flagship facilities that exist in the country. This results in training of students and scientists to develop skills with cutting edge knowledge. With complementary expertise, clearly defined research goals, common focus on deliverables and seamless communication between participants, such synergic activity would yield fruitful results and would also support education to provide future leaders in the field.

The aim of the bulletin on “BRNS Interaction with Research Institutes” with Dr.R.B.Grover, Secretary, BRNS, Director, Strategic Planning Group, DAE as the guest editor is to present a glimpse of BRNS initiatives to encourage the readers to approach BRNS for working in areas of interest.

IANCAS utilises NUCAR forum to support the aptitude in the young researchers in the filed of nuclear and radiochemistry by giving away cash awards and merit certificates for the best contributed papers. The deliberations in the NUCAR symposia have always been rewarding for the academics from the universities. There is enthusiastic participation from the universities in this symposium and it is reflected in the increased number of contributed papers.

The 48th BRNS-IANCAS National Workshop was organized at DDU University of Gorakhpur during October 19-28, 2002. Dr.S.B.Manohar, Head, Radiochemistry Division, BARC and President, IANCAS inaugurated the Workshop and gave a keynote address on the activities of Department of Atomic Energy. Prof. R.R.Pandey, Vice-chancellor of the university presided over the inaugural Function. IANCAS has also organized 5 one day Workshops in schools / colleges by giving lectures on Radioactivity and Applications of Radioisotopes and conducted demonstration experiment on half-life determination and shielding aspects.

Announcement inviting the nominations for Annual Tarun Dutta Memorial Award and Prof.Arnikar Best Thesis Award has received gratifying response and the awards will be presented during the NUCAR-2003 to be held in Mumbai during February-2003.

BRNS has been encouraging and supporting one of the major activities of IANCAS, namely organizing the National Workshops on ‘Radiochemistry and Applications of Radioisotopes’. IANCAS is grateful to BRNS for appreciating the publication of these thematic bulletins with generous grants every year.

G.A. Rama Rao

An Interview with
Shri B. Bhattacharjee
Director, Bhabha Atomic Research Centre (BARC)

*(Interviewed by Dr. A.V.R. Reddy, Editor, IANCAS and
Dr. S.B. Manohar, President, IANCAS on 14.12.2002)*



“..... various centres of excellence created within BARC need continuous replacement of high quality human resource not only for preservation of existing knowledge base but also for their upgradation for deployment in future technologies.”

Shri B. Bhattacharjee obtained his Master's degree in Chemical Engg., from the University College of Technology, Calcutta, and graduated from the 9th batch of BARC Training School in 1966. He has been the key person for successful implementation of the project presently known as Uranium Corporation of India Ltd, Jaduguda, which is the only uranium mill in the country. Afterwards, he switched over to multi-disciplinary R&D activities at BARC, Mumbai for development of High Speed Rotor (HSR) technology for production of strategic materials. Design, installation and successful commissioning of HSR technology enabled India to produce some of the materials of strategic importance. Spin-off to HSR technology has enhanced the country's engineering base in general and that of precision engineering in particular.

Presently, Shri Bhattacharjee is the Director, Bhabha Atomic Research Centre and Member, Atomic Energy Commission, Govt. of India. Shri Bhattacharjee is a Member / Fellow of various professional bodies which include Fellowships of the Indian National Academy of Engineering and Maharashtra Academy of Sciences. In recognition of his outstanding contributions, he has been conferred with coveted national award "Padma Shri".

1. On behalf of IANCAS and on our own behalf, please accept our New Year Greetings. We thank you for your support for IANCAS activities and also giving us this opportunity

to know your views on various aspects of R & D Programmes of BARC and the linkage between educational institutions and BARC.

Thank you very much for the New Year Greetings and let me also reciprocate by taking this opportunity to wish IANCAS a very active and professionally satisfying 2003. You are always welcome for any support any time for expanding IANCAS's programme. As you are aware, BARC is the largest research institute in the world where the widest spectrum of research and development activities are pursued under a common umbrella and BARC is committed to exploit nuclear science and technology for (a) improving the quality of life of our 1 billion plus population; (b) staying at the forefront of nuclear science and technology in order to retain the place of honour and dignity for India amongst the world community; and of course (c) enhancing the national security. For improving the quality of life in the society, our primary mandates are to: (i) provide energy security by way of generation of nuclear power that is safe, reliable and economical in addition to its eco-friendliness; and (ii) use radioisotopes and radiation technology in non-power sector for health care, industry, agriculture and food preservation, isotope hydrology, nuclear desalination, etc.

But harnessing nuclear energy for its utilisation either in nuclear power sector or non-power sector calls for development of a host of technologies which demands high level of excellence in both basic sciences and engineering sciences. In order to fulfill our commitment to exploit nuclear energy for the societal benefits, we have created centres of excellence at Bhabha Atomic Research Centre where scientists and engineers are pursuing excellence in basic science (in all the relevant areas of physics, chemistry and biology) while pursuing technology development tasks in mission mode. These pursuits are nurtured in complimentary mode to each other like the twin strands of DNA molecules. Once the technologies are brought to maturity at demonstration scale, these are subsequently deployed at commercial scale either by the various public sector units/industrial units under the Department of Atomic Energy (DAE) or by BARC itself.

Being the premier R&D institution in the country, in addition to providing all the necessary R&D inputs for all ongoing programmes like (i) development of various NDE tools for life extension; (ii) qualification of the fuel bundles through in-pile and out-of pile testings; (iii) establishing various fuel cycle facilities needed for expanding PHWR programme in the country along with (iv) development of technologies for fuel and fuel handling systems etc., for FBR programme, BARC has also the responsibility to develop the technologies for the future. In the context of future technologies, I must add that our top priority is development of technologies needed to induct new concepts of nuclear reactor systems like (a) our 300 MWe Advanced Heavy Water Reactor (AHWR) for establishing the expertise needed for generating nuclear power from thorium based fuel in an innovative reactor with safety features based on totally passive

systems, (b) to be followed by Compact High Temperature Reactor (CHTR) to introduce nuclear energy as primary source of energy (in place of electricity alone) for a variety of applications like production of hydrogen as an environmentally friendly alternative to hydrocarbon fuels for our transportation sector, desalination of water etc., and (c) Accelerator Driven Sub-critical System (ADSS) in the long run for accelerated growth for thorium based nuclear power which would also help in minimising the technological complexities involved in management of nuclear wastes. Similarly, we have assigned equal importance to take the benefits of radioisotopes and radiation technology for health care, industry, agriculture and food preservation, while pursuing our programmes on excellence in basic sciences, development of Parallel Processing Anupam Supercomputers, Cryogenics, Micro-electronics, Solid Oxide Fuel Cell, etc.

Coming to your question of BARC-Academia linkage, the various centres of excellence created within BARC need continuous replenishment of high quality human resource not only for preservation of existing knowledge base but also for their upgradation for development of future technologies. We are fully aware of the availability of young talents and wisdom of the faculty in the academia in the country. We must provide the frontline of science and technology to the University system and the faculty members/students community should update their knowledge base as per needs of research institutes/industries in a win-win situation. We have, therefore, plans for expanding BARC-Academia linkages (in addition to the in-house HRD programme) to establish ultimately a national network which will provide access to the entire academia in the nation about our knowledge base on nuclear science and technology to take advantage of, as I said earlier, the pool of high quality young talent and wisdom of the faculty members available in our university system through collaborative programmes. In fact, such interaction is also yet another way by which our scientists and engineers could upgrade and enhance their knowledge base. To my mind, IANCAS has an important role in this matter.

Further, through the wings of the Board of Research in Nuclear Sciences (BRNS), we constantly pursue various collaborative research programmes with the Universities in the most cost effective way which also includes setting up of major research facilities that provide an excellent training ground to the University students in the areas which are of interest to BARC/DAE.

2. Thank you Sir. We are happy that immediately after taking over as Director, BARC, you stressed the importance of dedication and hard work to achieve our targets. Will you please elaborate?

While I am quite happy with the prevailing level of dedication and hard work at BARC which is keeping BARC in the forefront of nuclear science and technology in the world, we also need to keep in mind that the results of our sustained R&D efforts over the decades in both power sector as well as non-power sector need to be taken to the society at a faster pace. In other words, it is time for consolidation and expansion of our achievements in various fields of nuclear

science and technology for the societal benefits. For this, all of us should get inspired by the concerns of our national needs and work harder with more dedication and sense of national pride.

3. *BARC is one of the institutes of its kind wherein expertise on a large number of R&D is available under one roof. For the benefit of members of IANCAS, would you please throw light on how the concept of the multidisciplinary center was conceived and nurtured?*

It has been recognised since our independence that India's national development would have to be driven by science and technology. It has also been recognised that it is not possible to transform the economy of a country on the basis of modern technology that has been developed elsewhere without establishing modern science and technology in the country at the same time. As Dr.Bhabha said "what developed countries have and the under developed countries lack is modern science and an economy based on modern technology". It was also clear about the inevitability of nuclear energy for a country like ours with very low per capita electricity consumption. Accordingly, right from the beginning of our programme, emphasis has been laid on dependence on indigenous nuclear resources and reliance on technologies developed in-house to exploit nuclear science and technology for sustained energy security, food security and health care in India. But as I said earlier, it calls for development of a host of technologies which are multi-disciplinary in nature and demands high level of excellence in both basic science and engineering science. Accordingly, the concept of BARC as a multidisciplinary research institute was conceived where scientists and engineers can pursue excellence in basic science (in all the relevant areas of physics, chemistry and biology) while pursuing technology development task in mission mode. In this context, I am indeed happy to state that one of the prime reasons behind India's success story in the field of nuclear science and technology has been the multidisciplinary nature of BARC where we have established centres of excellence in both basic and engineering sciences that are comparable to the best in the world.

4. *BARC has been the fountainhead for R&D inputs in all the spheres pertinent to our Atomic Energy programme. In your opinion, what are the major thrust areas where BARC has now to focus? Your views would be of immense help to members of IANCAS to understand the priorities of BARC.*

For the sake of clarity in understanding, let me identify the major thrust areas of BARC which need our focussed attention into the following broad categories, namely:

Sustained and concerted efforts to continuously upgrade the performance of all the existing nuclear facilities at the back end of nuclear fuel cycle and rapid expansion of such facilities to enable rapid growth of our PHWR programme. Development of advanced technologies for vitrification of high level liquid waste is important in this context. This also includes, as I said earlier, pursuit of

excellence in all the areas of basic sciences, successful completion of a large number of beam lines that we have planned at Indus-II facility at CAT, Indore, etc., development of techniques/technologies needed for life extension of our existing PHWRs and investigations for qualification of 500 MWe fuel bundles. In this category, I would also include our responsibility for developing technologies for supply of fuels, fuel handling and fuel transfer systems and establishment of the facilities for fuel fabrication at Kalpakkam for our Prototype Fast Breeder Reactor (PFBR) programme.

Simultaneously, our achievements in non-power sector involving applications of radioisotopes and radiation technology for health care, food preservation, industry etc., are to be taken to the society on high priority. This also includes early completion of the electron beam centre at Kharghar at Navi Mumbai that will provide the entire range of electron beam accelerators (500 KeV – 10 KW DC; 3 MeV – 30 KW DC; 10 MeV – 10 KW RF) to cover the entire need of the industries in the country.

We have plans for development of certain critical technologies like cryotechnology for production of liquid helium; enhancing the power of our parallel processing supercomputers from the existing level of 72 Gigaflops to 1 Teraflops capacity by the year 2005 and solid oxide fuel cell.



Induction of 300 MWe Advanced Heavy Water Reactor (AHWR) by creating facilities like (a) Critical Facility for experimental determination of the various reactivity coefficients and confirmation of the neutronics data used in the physics design at DPR level; (b) detailed studies with respect to flow stability, critical flux, flow induced vibration, ECCS response, performance of isolation condensers etc., in an Integral Test Facility to validate the computer models of two phase natural circulation flow related phenomena in AHWR; (c) development of fuel cycle technologies for fabrication, reprocessing and waste management of thorium based fuels.

Induction of nuclear energy as a source of primary energy in the society by way of developing a small Capacity [~200 KW(th)] High Temperature Reactor (CHTR) as a high temperature heat source (800-1000°C) to produce hydrogen from water by using thermo chemical means for transportation sector in the country. This involves development of a number of special technologies for fabrication of fuel (^{233}U carbide based), coolant (molten lead / lead of bismuth eutectic), moderator, reflector etc.

Finally, the stage-wise development of technologies for high power spallation targets, high power proton accelerators, and a sub-critical core for induction of Accelerator Driven Sub-critical System (ADSS), I was referring to earlier.

5. We are happy that you mentioned about AHWR. In view of our vast sources of thorium, it is commendable that we are developing the concept of Advanced Heavy Water Reactors to utilize thorium. For the benefit of IANCAS members, please tell us about the road map for the development of the required technologies and fulfillment of the realization of power from AHWR.

As I said earlier, induction of 300 MWe AHWR is our first priority in the area of new reactor concepts that have been conceived at BARC. AHWR is a vertical pressure type reactor based on thorium fuel (initially loaded with (Th-Pu) MOX to be followed by (Th- ^{233}U) MOX at a later date), using D_2O as moderator and H_2O as coolant. AHWR is first of its kind in the world that has the most attractive features of heat removal by natural circulation under normal as well as emergency situations and it incorporates a host of other passive safety features that are in line with the approach being followed world over for development of inherently safe reactor system with safety features that do not call for any human intervention or active control devices for reactor safety. About 65% of the total power developed in AHWR would be derived from thorium fuel. Detailed Project Report for this reactor is now being reviewed by peer groups consisting of professionals from NPCIL as well as specialists from BARC who are not directly involved in this programme. The technologies needed for fabrication of the initial fuel (Th-Pu) MOX, separation of ^{233}U by reprocessing of the irradiated fuel and refabrication of the (Th - ^{233}U) MOX fuel have been established at a pilot scale and we are confident that (Th- ^{233}U) MOX can be fabricated in our remote handling facility without major problem. We have also taken up the task of cleaning of ^{232}U from the separated ^{233}U by using laser separation technique and

within about 5-years time we should be able to establish technologies involved in thorium fuel cycle at a demonstration scale.

Meanwhile, the construction of the critical facility for AHWR is in progress which will be utilised for experimental verification of various reactivity co-efficients and neutronic data that have been used for physics design of AHWR. Similarly, an integral testing loop is being installed to study various aspects of two phase natural circulation flow at large scale for experimental validation of the various thermal and flow instability phenomena, if any, in AHWR. We expect to start construction of this reactor in about two years time and it is expected to be completed in about 7 years time thereafter.

6. *Thank you Sir. In our three-stage nuclear power programme based on a demanding, closed nuclear fuel cycle we are amidst the second stage, namely development of fast breeder reactor technology. What would be BARC's contribution in this direction?*

BARC has been involved as a supporting partner in development of fast breeder reactor programme right from the stage of establishing FBTR at IGCAR, Kalpakkam. However, BARC's major contribution in establishing PFBR would be in the area of development and supply of the entire first charge of PFBR fuel, its fuel handling and fuel transfer system.

In this connection, I would like to mention that uranium carbide fuel used at FBTR that has successfully reached a burn up of more than 100,000 MWD/Te was developed and supplied by BARC. However, our other commitment in this context is design, development, installation and commissioning of fuel fabrication facility at PFBR site that would enable PFBR personnel to undertake fabrication of subsequent fuels for PFBR. Various shielding experiments and neutron streaming experiments required for PFBR were also completed at BARC.

7. *You have mentioned "one of our major concerns is to improve quality of life by systematic induction of nuclear science and technology". It is indeed the need of the hour. Would you kindly give your plans as to how this could be achieved?*

As I stated earlier, we are committed to improve the quality of life in our society by (i) providing energy security by way of generation of nuclear power; and (ii) by using radioisotopes and radiation technology for health care, industry, agriculture and food preservation, isotope hydrology, nuclear desalination, etc.

We are aware, water, energy, environment and education are the essential pillars of the structure that support quality of life in the society in any country, particularly in the developing countries with large population like ours. The linkage between availability of sufficient primary energy in general (and that of electricity in particular) and the economic growth of the country is established beyond doubt. Our per capita electricity consumption is only about 600 kWh (which is less than one-fourth of even the world average value of 2500 kWh) compared to the target of about 5000-7000 kWh which is the bare minimum required for an acceptable quality of life in a society. Various means of energy

production and its consumption pattern in different sectors of the society have direct bearing on the environment because of their direct linkages with the generation of associated wastes. For sustained development of society, it is important to strike a balance amongst these life supporting pillars failing which the society will collapse sooner or later depending on the amount of imbalance we allow in the life supporting structure.

At present, fossil fuels particularly coal, plays a dominant role which accounts for about 70% of India's total electricity generation capacity of about 1,31,000 MWe (which includes about 27,000 MWe generated from captive power plants) followed by hydro sources accounting for about 25% share of generation capacity with a small contribution (of 3%) from nuclear source. But our fossil fuels are dwindling fast and their excessive use has already triggered the alarm bell of the danger of global warming arising out of emission of carbondioxide. Hydroelectric power sources, which are apparently eco-friendly renewable sources, are linked with undesirable effects of damage to natural environment (by way of inundation and submergence of vast areas of land) in addition to the difficulties associated with their locations in inaccessible areas. Other forms of renewable energy sources, though virtually inexhaustible are not suitable for electric power generation at their present stage of technological development. We are, therefore, left with no other option but to increase progressively the share of nuclear energy in the overall energy mix in India which can easily be observed, if we have a new look at the various options of energy resources available in the country.

For developing countries with large population like China, India and South Korea, where there is a wide gap between the prevailing per capita electricity consumption, and the certain minimum recommended for an acceptable quality of life in society, the growth of nuclear energy is very high. In India, we have 8 nuclear power stations under construction now.

Our 12 units of PHWRs (in addition to 2 earliest BWR units) are operating at world class level, both in terms of capacity factor (about 90%) as well as safety record. We are planning to increase the share of nuclear power from the present level of 3% to about 5% by the year 2008 and to about 10% by the year 2020.

Parallel to the world class performance of our indigenous PHWR plants, the growth of applications of radioisotopes and radiation technology in non-power sector has also been remarkable in India covering a wide spectrum, starting from nuclear agriculture and food preservagtion at one end, to health care and industrial applications at the other end.

Health care: In the area of health care, major emphasis has been assigned for diagnosis and prognosis in a variety of diseases as well as for providing relief by both curative and palliative treatment, details of which need no further elaboration to you.

To cope with the increasing demand, we produce (i) large quantities of 10-15 types of regularly used neutron rich radioisotopes in research reactors and

nuclear power plants; (ii) radioisotopes like ^{137}Cs , ^{90}Sr by separating them from fission products (FPs) and very recently (iii) we have added medical cyclotron (16.5 MeV proton beam) with PET facility at the Radiation Medicine Centre (RMC) at Mumbai for production of neutron deficient radioisotopes such as ^{18}F that will provide Fluoro Deoxy Glucose (FDG) for the patients. We have also planned to add a large medical cyclotron (30 MeV proton beam) with PET facility at Kolkata in the X Plan period to produce larger quantities of PET group of radiopharmaceuticals along with radio-nuclides like ^{201}Tl , ^{97}Ga , ^{111}In and ^{123}I which are otherwise not possible to produce with 16.5 MeV medical cyclotron facility at RMC that would provide opportunities to develop other radiopharmaceuticals.

Addressing the problem of providing of drinking water at an affordable cost to water scarce areas in the country, we have set up a desalination plant (1800 m³/d) based on reverse osmosis technology at Kalpakkam, Chennai which will soon be coupled with another plant (34500 m³/d) based on the multistage flash evaporation technology, making this nuclear coupled desalination facility a unique one to have hybrid technology.

Nuclear Agriculture: In the areas of nuclear agriculture, we have released 23 varieties of various crops for commercial cultivation by developing radiation induced mutants and their cross breeds. All these mutants are of high yielding variety while most of them are disease resistant also. At all India level, our 4-black gram varieties account for about 50 percent, while our 9 groundnut varieties account for about 30 percent of the total national breeder seeds indents for these two varieties respectively.

Industry: India is the lead country in industrial applications of radioisotopes in Asia & Pacific Region because of our excellence in all three areas of applications – (i) use of sealed sources (γ -radiography, computer aided tomography, γ -scanning & nucleonic gauging); (ii) use of open sources as Radio Tracers, (e.g. for RTD measurements for process optimisation in chemical, petroleum and petrochemical industry); (iii) radiation processing (using Electron Beam Accelerator, 2 MeV-20 KW-DC-type) for a host of applications out of which radiation crosslinked polymers/co-polymers for electrical cables/wires with improved electrical and mechanical properties (which are not possible to achieve otherwise). Very soon, we are going to add the entire range of EB-accelerators (500 KeV – 10 KW DC; 3 MeV-30 KW DC; 10 MeV-10 KW RF) to cover the entire need of the industries.

Food Processing: Radiation processing is fast emerging as an important technology for the preservation of agricultural commodities, hygienisation of food and sterilisation of medical products. It also provides a method for overcoming the “quarantine barrier” in the international trade of food products. Radiation processing, therefore, plays a major role in strengthening the food security of the country and in meeting the statutory requirements for international trade in food products. Starting with a Spice Irradiator (250 kCi ^{60}Co), we have also added very recently a POTON facility (10 Te/hr) for

preservation of onions by low dose irradiation (^{60}Co).

8. Thank you Sir. Now we switch over to a vexing question, but an important one in our programme. Not only the general public, but also educated ones are concerned about the radioactive waste management. We feel that this exaggerated concern is due to lack of proper information. Will you kindly explain the emphasis given and goals set in this programme by BARC and DAE?

At the outset, I must admit that the concerns expressed by the general public is quite justified particularly because of the facts that (i) power of nuclear energy has been introduced to the human society in its destructive form at Hiroshima and Nagasaki and also (ii) radiation is something that cannot be felt, seen or smelt by human beings. This concern has, therefore, to be allayed primarily through demonstrations of our technological capability that is completely safe and totally reliable to handle various types of radioactive wastes.

In this connection, I am happy to inform that India is one of the few countries in the world who have mastered all the technologies involved in management of various types of nuclear waste including the technology for vitrification of high level liquid waste (which is the major concerns of common people). I can assure you that the management of radioactive waste will not remain a cause for concern to the public and it will never come in the way of growth of nuclear energy in the country. Of course, we have future plans to develop better technologies for vitrification of high level liquid waste in the X Plan.

I may also add here that in addition to the special drives initiated at DAE/BARC, to allay such apprehensions due to misinformation/ignorance, the professional associations like IANCAS may strengthen our efforts by disseminating factual informations and the results of our R&D efforts to the public. I am personally aware that IANCAS is already making their valuable contributions in this direction – may be a bit more can be expected from IANCAS.

9. Thank you Sir for the confidence reposed in IANCAS. We are sure that BARC, under your able guidance, will strive to achieve the defined targets and look forward to re-define higher goals. Human resource development is one of the key factors for continuity and sustenance of the programmes. Our method of imparting training by working scientists and engineers is being appreciated. Would you please give some details about BARC Training School programmes?

Realising the ground reality that the success or otherwise of our multidisciplinary programmes for taking the benefits of nuclear science and technology to the Indian society depends mainly on the availability of sufficient number of high quality trained manpower, we have assigned top priority to our HRD programmes. To meet our needs in terms of human resource, we have devised a variety of programmes for training, some at the entry level and some during the service period to tackle obsolescence. At the entry level, our first programme is based on the principle of “hire and train” where we select graduates in engineering and post-graduates in science disciplines and train them in nuclear science and engineering for a period of one-year in four training

centres located at BARC, Mumbai; CAT, Indore; NFC, Hyderabad and NPCIL, Mumbai before assigning them to different units in the Department. Under our second scheme, we select engineers with post-graduate qualifications and train them for four to five months before their placement in different units for effective utilisation of the already mature Master's Degree Programmes in engineering at our academia. In our third scheme – "DAE Graduate Fellowship Scheme" – we select M.Tech students in various disciplines of IITs/IISc who are adopted by DAE during M.Tech course and finally absorbed by DAE. We have plans to extend this programme to other leading Universities in the near future.

Under Dr.K.S.Krishnan Research Associateship, research associates are inducted every year for a two-year Associateship with the possibility of getting them absorbed, depending on their performance, in one of the R&D organisations of the Department.

In parallel to the various induction programmes, we also place considerable emphasis on future upgradation of qualifications of our scientists and engineers. We encourage them to pursue Masters Programme in engineering as well as register for advanced degrees based on the work done in our research centres.

10. Sir, Thanks for your lucid explanation. In fact, the process of selection of trainees itself is unique. While talking about training, we would like to know what are the efforts by BARC, being a premier institute of R&D, to provide quality training to others, particularly from Universities?

In addition to our in-house training programmes, we have a series of other programmes to train personnel from outside DAE family – particularly those from the University system through (i) class room lectures and laboratory experiments, (ii) participation of students to work towards M.Tech or Ph.D programmes, (iii) training in specific areas like radiation safety and non-destructive testing (NDT), (iv) training in safe handling of radioisotopes and (v) training in radiological emergency preparedness etc. For training in first category, faculty members are drawn from BARC, IGCAR, BRIT, etc., to organise awareness programmes and workshops through Associations like IANCAS and NAARI. Under the second category of our training programmes, students from the university system utilise some of our major experimental facilities under the guidance from our experts to work towards their M.Tech and Ph.D programmes. In addition, BRNS has various schemes under which the students community are provided with facilities to undergo training programmes in various aspects of nuclear science and technology.

11. Some light on the training programmes in the safe handling of radioisotopes and other of training programmes that are being conducted by BARC.

In the context of training in safe handling of radioisotopes and other activities involving radiation technology, I must make a mention of some of the training programmes in this area that are specially designed to cater to the safety requirements while using radioisotopes/radiation technology in medical,

industry and agriculture applications, namely, (i) BARC organises an exhaustive four week long training programme for operators of food irradiation facility in collaboration with BRIT on various aspects of radiation safety in handling and transportation of radiation sources, radiation dosimetry, medical management of radiation emergencies on the one hand and quality control in food irradiation, safety and wholesomeness of radiation processed foods, radiation processing of food for preservation and hygienization and plant management; (ii) BARC is the prime centre in the country that has been imparting one year post M.Sc Diploma course in Radiological Physics since 1962 in collaboration with University of Mumbai. BARC provides quality services pertaining to radiation safety, quality assurance and dosimetry for radiotherapy centres. These Diploma holders are eligible to apply for the post of Radiological Safety Officer in the Hospitals and Industries; (iii) Radiation Medicine Centre (RMC) has been catering to the HRD in nuclear medicine by conducting course on “Diploma in Radiation Medicine (DRM) for Doctors and “Diploma in Medical Radioisotopes Techniques (DMRIT) for technologists. The vast majority of the nuclear medicine personnel in India have been trained in this. Training in the field of RIA was started by BARC in 1982 and has been a very successful programme and 1000 medical and paramedical personnel have been trained in 42 batches. At present, there are over 500 RIA laboratories in India, thanks mainly to RIA programmes conducted by BARC. BARC has also trained 40 personnel from 20 countries under RIA programme of IAEA; and (iv) BARC also provides training in the areas of radiation hazards and radiation control to the personnel from army, navy, police, customs etc., as part of our training programme on “radiation emergency preparedness”.

12. As you are aware, IANCAS has been working to spread the awareness on the beneficial uses of radioisotopes and Atomic Energy Programme. As a well-wisher and supporter of IANCAS activities, do you have additional suggestions for IANCAS in this regard?

It is well recognized that IANCAS is doing an excellent work in this direction. I am glad to inform you that there is lot of demand for your programmes and I receive quite a few requests. I suggest that even if there are some difficulties, these programmes should be pursued. Wherever you conduct a Workshop, please do not hesitate to leave the instruments and associated facilities to the host institution to encourage the sustenance of nuclear sciences in the universities. I compliment the members of IANCAS for their efforts in this direction and urge them to increase the activities. IANCAS programmes will be supported.

13. Thank you Sir, for your appreciation and continued support. Members of IANCAS would strive to implement your suggestions. Now we seek your views on another important area: collaboration. IANCAS members would be privileged to know how BARC would support the universities in this regard?

As I have indicated earlier, the various centres of excellence created within BARC need continuous replacement of high quality human resource not only for

preservation of existing knowledge base but also for their upgradation for deployment in future technologies. The best way to tackle this problem is to ensure availability of young talents and wisdom of our faculty members in our university system through collaborative programmes in various areas of nuclear science and technology. In this context, I must mention that half life of knowledge base of scientists and engineers is about 5-6 years unless it is updated regularly in all aspects of science and technology. The scheme of collaborative programme is the most cost effective way for providing this opportunity to work in frontier science and technology while we utilise the pool of high quality talents and wisdom of faculty members of the university system to solve some of our problems. On one hand, such collaborative programmes would require the faculty members of University system to upgrade their knowledge base, such programmes are yet another way by which our own young scientists and engineers could upgrade their knowledge base in a win-win situation. We, therefore, provide all possible supports to such activities under various schemes.

14. One of the major problems in the universities is funding to initiate and sustain R&D in newer and frontier areas of Science and Technology? Could you please tell us about the role of BRNS in this direction?

We are aware of the problems being faced by our university system. Accordingly, DAE supports R&D activities at the University level through BRNS, which is one of the oldest funding agencies in the country. It is chaired by eminent scientists/engineers and there are 4 Advisory Committees that look into various proposals from university system/research institutes for recommendations for grant of research funds to BRNS and monitor progress of such research activities through the concerned participants from DAE family. In addition, there are a large number of scholarships and research associateships available under BRNS scheme to address some of the problems being faced by the University system.

15. Many thanks for the details Sir. You have been associated with BRNS activities as Chairman of Nuclear Reactors and Fuel Cycle Committee, apart from your current role in BRNS as Director, BARC. Would you kindly give your views on the efforts from BRNS and the returns in terms of quality research and trained manpower?

BRNS has been performing a commendable role by providing progressively stronger and stronger linkages of the university system/research institutions in the country with DAE programmes. In addition to extending the financial and technical support (by way of utilisation of facilities in DAE units) to various academia and research institutions to pursue excellence in basic science as well as engineering science in the areas of interest to DAE. BRNS has also succeeded in establishing a number of high quality research facilities in the country through which we can utilise the talents available in academia/research institutes for carrying out research activities in the areas of interest to us. Further, these

research facilities also help us to give improved training to our scientists and engineers.

Some of these major research facilities that have been created through BRNS are:

(i) The Free Radical Research Facility at the University of Pune; (ii) Seismic Research Facility at the Structural Engineering Research Centre (SERC) at Chennai; (iii) Facility for equipment testing at high temperature and high pressure (simulating certain accident conditions in nuclear reactors) at ERDA, Baroda; (iv) Facility for development of radiation resistance of glasses at CGCRI, Kolkata; and (v) Centre for Formal Design & Verification of Softwares at IIT Mumbai. We are also setting up some advanced centres, for example, Centre for Thermal Hydraulics for AHWRs at IIT, Mumbai and Centre for Knowledge base Design & Engineering at UICT, Mumbai, dedicated to DAE programmes. These centres not only enable our programmes to benefit from the expertise available with the University system but also provide a very valuable training ground to the university students in the areas which are of interest to us.

In fact, through such major facilities, academic/research institutes should participate in our programmes on AHWR, FBR, ADSS etc., in a concerted way, i.e., they should involve various disciplines in a joint multi-disciplinary effort instead of the present practice of working on DAE's programmes from a particular department in isolation. Academia should also consider allowing students from various disciplines to utilise such major facilities for doing their M.Tech/Ph.D programmes simultaneously. This needs to be discussed with institutes/universities further. In fact, through such multi-disciplinary approach, contributions from the Universities and other research institutions can be expected to grow for our major programmes like AHWR, FBR and ADSS.

16. *One of the key drivers proclaimed by Chairman, AEC is "Mutual strengthening of education and research in nuclear sciences...". Would you kindly elaborate the efforts of BARC in this direction?*

For pursuing excellence in basic research, we provide large experimental facilities such as Research Reactors and Accelerators at Mumbai, Synchrotron and Laser Sources at Indore and Cyclotron at Kolkata to the Indian scientific community to carry out their research activities in collaboration with DAE scientists. The Inter-University Consortium for DAE Facilities (IUC-DAEF) which came into existence in 1989, is working towards this goal. Further, we also strengthen the synergy between BARC/DAE by providing assistance to the institutions of national eminence in basic and applied research. As indicated earlier, through the wings of BRNS, we strive to pursue various collaborative research programmes in the most cost effective way with the Universities and research institutions.

17. *In your opinion, what magnitude of contributions from Universities and other research institutions can be expected to our major programmes such as AHWR, FBR, ADSS and radioactive waste management?*

In all these programmes, Universities and other research institutes can play a significant role in all areas which do not involve handling of radioactivity and also in the areas where the radioactive material can be substituted with a simulated and sarogated material. In fact, the Universities and research institutes should be approached to handle progressively bigger and bigger programmes and some of these programmes in a multidisciplinary way.

18. *In fact in the areas of R&D pertaining to Agriculture, contributions from the universities are well appreciated. Do you envisage any other area for a similar progress?*

In the areas of nuclear agriculture, we have released 23 varieties of various crops for commercial cultivation by developing radiation induced mutants and their cross breeds. These mutants include 10 of pulses (4 black gram, 4 green gram and 2 pigeonpea), 9 of ground nuts (the latest entry of which – TG-41 – a special mutant of large seeded variety for confectionary purpose); 2 of mastard and 1 each of jute and rice. Most of these mutants are of high yielding variety while quite a few of them are disease resistant also. At all India level, our 4 black gram varieties account for about 50 percent of the total national breeder groundnut varieties account for about 30 percent of national indent. In fact, this year's indent for TAG-24 variety has made it to occupy the first rank among the 33 groundnut varieties. One of the major factors for our success in the area has been our linkage through MOUs with Agricultural Universities for dissemination of the results of our R&D efforts. In this connection, I would also like to add that we are working to expand our programme on breeder seeds production through the National Seeds Corporation, Delhi, to cope with the increasing demand of our mutant varieties.

19. *It is generally felt that collaborative efforts should be carried out as partners in progress rather than driven by a single institute. What are your views on this concept?*

Yes, I fully agree with you. Once the mutual benefits to the partners involved are established (which I have explained earlier) the programme has to be pursued entirely in collaborative mode where both the investigators from the academic/research institutes and the DAE collaborators must shoulder the joint responsibility for the success of the programme. Further, DAE collaborator must also have the added responsibility to ensure that the collaborative project has actually achieved its objective so that the same could be utilised at DAE in handling similar problems of ground reality (instead of the results remaining in the archives).

20. *It is believed that substantial contributions from young and enthusiastic members could be obtained if the facilities in the premier institutions are open to them. We feel that the DAE-University fellowship programmes with Mumbai University and University of Pune are major steps in this direction. Do you envisage more schemes like-wise?*

As I said earlier, we must make use of young talents and wisdom of faculty members available in the University system in a win-win situation. However, esssentially such linkage should grow around a major unit of DAE like BARC, IGCAR, CAT and VECC on the basis of our strengths and inputs needed for our

programme on one side and the corresponding strengths and interests of the academia/research institutes on the other side. Otherwise, it will be difficult to sustain such major programmes. In this context, I may add that we have plans to expand some of our activities at BARC to some other location, which I am sure, would act as yet another centre for such activities to grow.

21. Thank you Sir. IANCAS has always been striving to provide a forum for information exchange between DAE, users of isotopes and university academia. We have been fortunate in receiving continuous support from the Department. We seek your valuable guidelines for widening and for more effective implementation of IANCAS programmes.

IANCAS activities are highly appreciated both inside as well as outside DAE family. In fact, I must thank IANCAS for helping us in establishing the network of our knowledge base in nuclear science and technology across the length and breadth of the country through its Workshops and publication of quality thematic bulletins and books. I particularly appreciate the efforts undertaken by IANCAS in organising some simple and yet elegant experiments which not only provides information but also generates excitements / instill confidence among the participants about the various uses and safe handling of radioisotopes. Since most of the participants are teachers, it would always have the multiplier effect of spreading awareness about the beneficial aspects of nuclear energy, in addition to creating enthusiasm in nuclear science and technology through discussions during the lecture sessions of IANCAS's workshops. However, may be I can add a few suggestions. You should try to expand your activities by getting more and more teachers involved from progressively larger number of Universities into this programme and then identify some of the Universities with potentials to act as regional centres for doing this job for IANCAS. After initial period of assistance and training of the faculty/students at such institutes, you may leave behind some of the equipment and other facilities to enable them to carry forward this task voluntarily. This may, in some cases, involve some financial assistance to be extended to IANCAS. I am sure such assistance can be organised from our Department as long as IANCAS does shoulder the responsibility for the overall effectiveness of such activities. Since you have a large body of members from all over the country, formation and sustenance of such nation wide activities with Department's support should be a reality.

22. Thank you very much, Sir. We are indeed indebted to you for spending your valuable time and giving your views on various issues and programmes. On behalf of IANCAS, we take this opportunity to wish you a very fruitful and professionally rewarding New Year 2003.

It is my pleasure and thank you very much for your keen interest in promoting nuclear science and technology for our societal benefits. I also take this opportunity to wish all the members of IANCAS a Very Happy New Year 2003.

BRNS Interaction with Research Institutes

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Basic Sciences Committee (BSC)

“No country which wishes to play a leading part in the world can afford to neglect pure or long term research” Homi J. Bhahba

As basic science of today is the foundation for technology of tomorrow, the Basic Sciences Committee (BSC) of BRNS attaches a strong importance in selection of projects which are excellent and relevant to DAE mandate, covering chemical, bio-, physical, material and environmental sciences. BSC also plays a significant role in establishing fruitful partnership and strengthening linkages with universities and educational institutions. In the last few years the emphasis in BSC has shifted to approval of projects more on theme based thrust areas which are of current interest to DAE in general.

Keeping in mind interdependency of basic research and technology development, BSC plays a catalytic role in identifying projects which have the potential to evolve into technologies.

Some of the frontier areas recommended recently for BRNS funding by BSC are: Unique Catalysts, solvent extraction, radiochemistry, radiation and photo chemistry, actinide chemistry, laser induced chemical reactions, thin films and nano-materials, conducting polymers, molecular dynamics, nuclear structure near drip lines, incomplete fusion of stable and weakly bound projectiles, modifiers of radiation effects, cellular signaling, cancer research, protein structure and function, novel materials etc.

BSC has also carried out coordinated research programmes involving multi-institutes.e.g. Radon –Thoron mapping of India, Malformations and Down Syndrome in India are some of the programmes which have been completed in the recent years. Typically around 35 projects per year are recommended by BSC for funding by BRNS and the budget per project is on the average Rs.15 lakhs. One of the major funding for a facility has been the setting up of a national centre for free radical research at University of Pune.

BSC has adopted a practice to organise a Progress Review Meeting twice a year to monitor and review some of the ongoing projects which have made a substantial progress. BSC has contributed in a significant way to the selection of candidates for the DAE – young scientist award scheme. Most of these awardees are from the basic science stream.

Dissemination of information and discussion of results of R & D in open meetings is an important activity for the promotion of science and technology. For this purpose DAE – BRNS symposia/conferences etc are regularly organised annually or biennially in the field of nuclear, solid state, high energy physics, nuclear and radiochemistry, radiation and photo-chemistry etc. the thrust areas of DAE in the larger interest of the scientific community. A large number of conference requests are processed at BSC received from Professional bodies, institutes, universities, aided institutes of DAE in wide areas covering the discipline of BSC. Typically 40 to 50 conferences are funded by BSC. The number of projects recommended by BSC and the conferences processed by BSC is nearly half of the total handled at BRNS.

A synergistic collaboration between BRNS and IANCAS has resulted in the organisation of BRNS – IANCAS workshops on radiochemistry and applications of radioisotopes at different universities and educational institutions with a view to spread the knowledge in the field of nuclear science and technology and to improve the status of teaching and research in nuclear chemistry. It is a credit of IANCAS that to-date nearly 46 such workshops have been organised under this scheme.

From the wide spectrum of activities as summarised above, it can be seen that BSC has been nurturing innovative ideas, creativity in R and D and maintenance of proper ambience in all its endeavors. To sum up, the mandate of BSC forms the first step of “R3D- Research, Development, Demonstration and Deployment” vision of Chairman, AEC.

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D.D. Bhawalkar

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Advanced Technologies Advisory Committee (ATAC)

The efforts of last four and half decades have enabled the Department of Atomic Energy to gain considerable maturity in all facets of nuclear technology on par with the developed countries. The acquisition of the related sophisticated technologies has been made possible by a synergistic combination of research in basic and applied sciences on the one hand and development of cost competitive advanced technologies on the other, in spite of the denial of access to advanced science and technology because of our principled stand on NPT. This denial blessed us with many relevant advanced technologies, supported by multidisciplinary expertise, a community of highly competent scientists and engineers, and an unrivalled infrastructure. The rest is history.

Today there are new challenges again due to the globalisation of economy in the highly competitive environment and the technology control regime. The fact that these so called dual use technologies are required to deploy the scarce resources in a developing country more efficiently for the benefit of the entire population, has been the driving force for the DAE to support the development and growth of the advanced technologies.

For consolidating the gains made so far, and maintaining the creative output, the Board of Research in Nuclear Sciences, through its Advanced Technologies Advisory Committee, reaches out and supports the high tech R & D community in the academic and research institutions. This is sought to be attained through several mission oriented focused R & D projects in the area of lasers, accelerators, nuclear fusion, computers, cryogenics, materials and other advanced technologies.

Lasers have a wide range of applications in material processing, photochemical and photo-physical processes, communication, industries, medicine, defence, environment monitoring and pollution control, nuclear technology and research in physical and biological sciences. High selectivity achieved by laser based photo processes is used, with advantage, in production of several nuclear grade materials, which have to be isotopically tailored or cleaned to a very high purity. For these numerous applications lasers are required in powers ranging from microwatt to terawatt, in wavelengths range encompassing X-rays to microwave, and having pulse lengths from femto seconds to cw. Today diode pumped solid state lasers have revolutionised system diversity, conversion efficiency, and beam quality, and are considered the most significant development in lasers in two decades. BRNS has been supporting activity of building lasers for sophisticated applications, such as laser cooling and nuclear fusion studies, preparation of laser host materials, bulk and thin film ceramics and glass, and device making technology from the semiconductor laser wafers. Some of these projects such as production of Nd doped phosphate laser glass and preparation of laser dyes have resulted in industrially realisable technologies. Cancer diagnosis, related database generation in a multi-centric manner, photodynamic therapy of Multi Drug Resistant Tuberculosis are some of the thematic projects of Advanced Technologies Committee which have made a mark in various hospitals across the country.

Since accelerators and plasmas are essential tools for nuclear physics investigations, DAE has established a comprehensive expertise in the field of accelerator technologies, as well as in research using

high-energy beams. The accelerators have now applications in industry, medicine, material development and studies in atomic and molecular physics. BRNS has established a Centre of Excellence in Radiation and particle physics studies at Mangalore University, built around the 10 MeV Microtron, made by CAT, Indore. The accelerators are dependent on the technology of the high power switches, namely, Magnetrons, Thyratrons, and Klystrons. ATC, BRNS has funded and actively supported projects for the development of the switches and proving the technology with limited production at a CSIR laboratory. Successful demonstration of the Long Trace Profilometer for the mirrors of Synchrotron, and making of the white light interferometer for testing the synchrotron optics, are examples of the targeted approach BRNS has taken for development of relevant and at the same time cutting edge technologies. Linear motor driven cryo-cooler, cryo-cooled High T_c super conducting shield for SQUIDS, and equipment for housing the SQUID are some of the projects in the cryogenics. This list will grow in future.

The ANUPAM parallel computers, with its several versions have been one of the major technology contributions of DAE to the nation. BRNS projects have boosted these efforts by funding projects on the parallel file database, auto paralleliser, development of fast solver in the parallel environment, etc. Several CFD projects of BRNS for crystal growth, for ADSS windows, involving high end computing, are based on the contemporary versions of ANUPAM parallel machines.

One of the main applications of the automation and robotics in DAE

(D.D. Bhawalkar)
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Dr. Sreekumar Banerjee

Chairman, NR&FC Committee, BRNS

Director, Materials Group

Nuclear Reactor and Fuel Cycle Committee (NR&FCC)

The Board of Research in Nuclear Sciences (BRNS) under the Department of Atomic Energy (DAE) sponsors every year a large number of R&D projects to the leading academic / research institutes in the country in several advanced areas of interest to the department. The projects in the area of nuclear reactor technology and the fuel cycle are selected, reviewed and monitored for their annual progress by the Advisory Committee on Nuclear Reactor & Fuel Cycle (NRFC). This committee has been constituted by the DAE and comprises leading experts from the wider areas of research in the subjects under its purview. Besides this, the committee is also responsible to recommend to the Board the financial assistance for the non-departmental events such as International / National conferences, seminars, workshops and courses on several relevant advanced topics organized in the country by different institutions / universities. One of the main activities of the NR&FC committee has also been to initiate and monitor the organization of series of departmental annual/bi-annual conferences on different theme topics.

There are currently about 55 ongoing sponsored R&D projects under the purview of the NR&FC committee with the total annual funding to the tune of Rs 1 crore to 1.5 crore. The total funds sponsored to the individual projects varies in the range of Rs. 10 lakhs to about 60 lakhs depending upon the nature of studies proposed under the project and its duration. The projects cover several advanced topics such as experimental/analytical structural mechanics, fracture mechanics, vibrations analysis, thermal-hydraulics, heat transfer, chemical/bio-chemical reaction engineering, waste management, nuclear reactor safety, materials / alloy development for high temperature applications, corrosion and erosion studies, electrical and electronics related developments etc. Each project has an identified link to the departmental program and well defined deliverable every year on the part of both the Project Investigator (PI) and the Project Collaborator (PC). The project execution at the PI's institute and the PC's institution is thoroughly monitored by the committee with the help of experts from outside in an open forum such as Technical Project Discussion Meeting (TPDM) held annually.

Some of the high impacts made in the technology / resource development through the projects under NR&FC committee are as follows:

- Successful establishment of the Test set-up at a cost of about Rs. 1 crore for LOCA qualification of various components used in the nuclear power plants at ERDA, Vadodara and identification and implementation of a long term testing program in collaboration with the NPCIL.*
- Successful completion of the SITAC project at IIT, Bombay under which a test facility costing about Rs. 1.15 crore has been erected and commissioned for the purpose of fatigue testing of various structural elements/components used in the PHWRs and the proposed AHWR*
- Setting up of an advanced seismic test facility at the SERC, Chennai at a cost of Rs. 19.46 crore comprising of two shake tables of different capacities ranging from 5 Te to about 50 Te for the purpose of testing of various components for their seismic qualification.*

- *A group of eight different projects at different universities to study the thermal ecology related issues are nearing completion. The studies are carried out at two different sites of operating NPPs viz. Kaiga Atomic Power Plant and MAPS and one proposed site for the NPP viz., Kudankulam (KK) Power Project. The joint studies on these projects underway at different universities and costing about Rs. 1.2 crore are expected to be completed by March 2004 and should provide important data to frame national guidelines by the Ministry of Forests and Environment (MoEF) on thermal plume discharges from the power plants (including NPPs) into natural water bodies.*
- *Establishment of a Center for Formal Design and Verification of Softwares at IIT Bombay at a total cost of Rs. 3.1 (CFDVS) for the purpose of development of softwares and tools for software verifications. Being one of the highly advanced areas of research, the center has been successful in completing several internal R&D projects with the help of about 15 students mostly at M.Tech level. The center is also successfully exploiting the usefulness of one of the first unique facility of this type in the country by executing outside projects on commercial basis. In this respect while one project from ADA, Bangalore has already been successfully executed, the other one for the Texas Instruments (TI), Bangalore is currently underway. In addition, two new projects for the ISRO are under active consideration.*

The NR&FC committee under its purview has started, from the year 2002, holding of a series of conferences on nuclear reactor technology and fuel cycle every alternate year. The first of the conferences in the series was held in November 2002 at BARC with a theme topic as Nuclear Safety. The next conference in the series of Fuel Cycle has been planned on Nuclear Fuel Cycle and will be held at IGCAR towards the end of 2003.

The NR&FC committee by way of executing several sponsored R&D projects and by supporting a large number of national / international events of technical importance is supporting the aims and objectives of the BRNS very actively. With the more and more ambitious plans under consideration of the DAE under the Xth plan in the areas such as AHWR, PWR, HTR and ADSS, the committee is planning to do its best to exploit the potential of various schemes of BRNS in take up the frontiers of R&D to various potential academic/R&D institutes in the country.

(S. Banerjee)
Chairman, NR&FC Committee

(N. Markande)
Member-Secretary, NR&FC Committee



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N. Ramamoorthy

Chairman, RRT&A Committee, BRNS
Chief Executive, Board of Research in Nuclear Technology and
Associate Director, Isotope Group, BARC

Radioisotopes, Radiation Technology and Applications Committee

Board of Research in Nuclear Sciences (BRNS) has emerged over the years, as a unique institution for strengthening the bond between DAE and the scientific/technological talent available in the rest of the country. The key objective has been to encourage and promote scientific research in groups outside DAE family such as universities, institutes of higher learning and national laboratories in the fields relevant to the mandate of DAE and to derive synergistic benefit from collaborations. In order to meet the objectives of BRNS, the Advisory Committee for Radioisotopes and Radiation Technology Applications (RTAC) primarily focuses on research and development proposals related to technology of production and testing and also for development of techniques for applications using radioisotopes and radiation technology in the areas of healthcare, agriculture, industry and environment. The aim is to encourage demonstration and deployment of applications of societal impact.

Being a predominantly agriculture based country, application of radiation and radioisotopes in agriculture sector has been extremely important to RTAC especially in the areas of improvement of crop yield, insect/pest control and post-harvesting management of food. The nature of projects supported by the Committee cover a broad range of areas such as development of high yielding and disease resistant mutant seeds, radiation processing of food, development of radio-pharmaceuticals for specific applications, radiation processed drug delivery systems, use of radioisotopes for optimizing the use of fertilizers, use of radioisotope techniques for trouble shooting and process optimization in industries, development of polymeric formulations for radiation crosslinked wire and cables and heat-shrinkable products. In the last 3 years, the Committee has accepted 38 project proposals with an overall financial assistance of about 473 lakhs.

Committed to ensure that the fruits of R&D benefit reach the society, RTAC has always endeavored to create an environment in which professionals working in different areas of expertise can collectively work together to meet the challenges of bringing in the new technology in different sectors in the country. This will be evident from the fact that besides the regular project proposals from individual scientists, the committee has helped in development of following projects :

- In order to generate the expertise required to develop electron beam (EB) crosslinked wire & cable insulation materials indigenously, a joint project among IIT, Kharagpur, BARC and NICCO Corporation as industrial partner was formulated and successfully completed. The expertise generated and the experience gained in the project culminated in the NICCO Corporation setting up the first EB accelerator in the country for producing crosslinked wire & cables and heat-shrinkable materials. Sriram Institute for Industrial research, working on a similar project, developed formulations for crosslinking of poly vinylchloride (PVC) by EB irradiation for use as wire and cables with enhanced temperature of operation.*
- The data analysis of flow systems studied using radiotracers by measuring residence time distribution (RTD) pattern in many industries requires critical analysis by mathematical models. Under a joint project between University Institute of Chemical Technology (UICET), Mumbai and*

BARC, a window based RTD analysis software system has been developed and is being validated. The project will provide user friendly software to Indian industries for analyzing complex dynamics of the flow of the system.

- *A multi-location program on “Management of Red Palm Weevil by Sterile Insect Technique” is being concurrently pursued by 3 Principal Investigators at 3 different locations.*
- *Development of radio-pharmaceuticals with novel protecting groups for thiolate function for different ^{99m}Tc binding ligands is under progress at Indian Institute of Chemical Biology, Kolkata in collaboration with BRIT, Mumbai.*

In recent years, the Committee has also helped BRNS in formulating “Memorandum of Understanding” (MOU’s) with 3 different Universities to create new Centers for developing/deploying applications of radioisotopes.

1. *Setting up of a “Veterinary Nuclear Medicine Centre at Bombay Veterinary College, Parel”. This Centre would be the first of its kind in Asia, with a state of the art gamma scintillation camera for providing diagnostic facility for veterinary use, radiopharmaceutical research and for providing training to veterinary post-graduates in the field.*
2. *“Establishment of a Radiotracer Laboratory at Rajasthan Agricultural University” for using the radioisotope techniques in crop improvement and for testing BARC developed varieties of Mustard and groundnut under harsh desert climate.*
3. *“Establishment of Radiotracer Laboratory at College of Agriculture, Jabalpur and Multilocation Testing of BARC Crop Varieties”. Under the MOU, Jawaharlal Nehru Krishi Vishwa Vidyalaya, Jabalpur is involved in development of radiation processing as a post harvest technology for increasing the storability of regional fruits and vegetables and for multilocation testing and seed multiplication of BARC crop varieties of mung and urid by JNKVV.*

As a developing nation with the need to judiciously utilize the limited science fundings, we must focus on the area of critical need and pool resources to achieve the desired objective of national development. It is hence a solemn commitment at RTAC, BRNS that scientific development should reach the end users and must benefit one and all in the society.

(N. Ramamoorthy)
Chairman, RTA Committee

(S. Sabharwal)
Member-Secretary, RTA Committee

Guest Editorial



The history of the Board of Research in Nuclear Sciences (BRNS) is as old as that of the Atomic Energy Programme. Atomic Energy Committee, BRNS in its original form, was set up in 1945 under the aegis of the Council of Scientific and Industrial Research (CSIR) with the following terms of reference:

- (i) To explore the availability of raw materials required for generating Atomic Energy,*
- (ii) To suggest ways and means of harnessing the materials for production of Atomic Energy, and*
- (iii) To keep in touch with similar organisations functioning in other countries, and to make suggestions for coordinating the work of this committee on an international basis.*

With Dr. Homi J. Bhabha as its Chairman, this committee included Prof. M.N. Saha, Dr. D.N. Wadia (Mineral Adviser to the Central Government), and Dr. S.S. Bhatnagar (Director, CSIR) as Members.

Subsequently, the Atomic Energy Committee was re-designated as the Atomic Research Committee (ARC). ARC held its first meeting on 15th May 1946. The Press Note issued after the first meeting of the ARC stated, “Among the general recommendations of the Committee are the strengthening of the existing centres of atomic research, the selection of Tata Institute of Fundamental Research (TIFR) in Bombay as the Centre of all large scale programmes of atomic research in future and the holding of an annual conference in Bombay or Calcutta of workers engaged in atomic research”.

Once the Atomic Energy Commission came into being during 1947-48, the Atomic Research Committee was reconstituted as Board of Research in Atomic Energy (BRAE). It was the firm conviction of Homi Bhabha, as well as of his eminent colleagues in the ARC named above that “fundamental research and teaching should be fostered in the Universities and research institutes”. With the advent of the Atomic Energy Commission, BRAE came to be looked upon as an advisory body with the responsibility to “advice about the distribution of grants to the Universities and research institutes”.

BRAE held, in all, 12 meetings between 1947 and 1954 at the end of which, in the year 1955-56, BRAE was replaced by the Board of Research in Nuclear Sciences (BRNS). To start with, it had three Advisory Committees, namely, the Chemistry Advisory Committee, Cosmic Research Committee and the Biological and Medical Advisory Committee. As the activities of DAE grew, BRNS kept pace and by 1973 it had eight Advisory Committees to deal with various disciplines. In the early years, the BRNS or, for that matter, its precursor BRAE, was the only agency in the country that was funding research projects in the Universities. This unique position held by BRNS changed soon with CSIR extramural research becoming available, and especially with the creation of Department of Science and Technology (DST). DST has presently grown into a major government department extending research support to all branches of Science and Technology. In the light of this development, research funding by BRNS could be directed more towards research relevant to the needs of the Department of Atomic Energy. A sharper focus in this direction was sought to be achieved when in 1998 the number of Advisory Committees of the BRNS was reduced to four.

The renamed four Advisory Committees that cater to four different areas, are:

- *Advanced Technologies Committee (ATC)*
- *Basic Sciences Committee (BSC)*
- *Nuclear Reactors and Fuel Cycle Committee (NRFC) and*
- *Radiation Technology and Applications Committee (RTAC)*

The Chairman, Atomic Energy Commission mandated BRNS, and the four Advisory Committees, to develop research projects in centres outside the DAE, academic institutions and national laboratories, in a way as to complement and fortify research endeavours in the DAE units in fields selected to promote nuclear research and nuclear power programmes. It was added that, notwithstanding this thrust, outstanding research and researchers in basic sciences will continue to be spotted and supported through the Basic Sciences Committee.

This bulletin gives a glimpse of programmes of BRNS and we hope will encourage the readers to approach BRNS for working in areas of interest to DAE. DAE interacts with the institutions outside DAE in several ways and an article titled, “Alliances for R&D” summarises all such interactions. The remaining articles have been selected to provide a glimpse of work done under funding from BRNS.

In the end, I thank Dr. A.V.R. Reddy, Editor, IANCAS Bulletin for having given me this opportunity to explain the activities of BRNS to the readers of this Bulletin. I would also like to thank the Programme Officers of BRNS viz. Dr. P.P. Chandrachoodan, Dr. G.R. Relhan and Dr. Sunil Trehan for all the help given by them.

R.B. Grover

Alliances for R&D



Dr. R.B. Grover is a mechanical engineer working with the Department of Atomic Energy, Mumbai for over three decades. He graduated in mechanical engineering from Delhi College of Engineering and received doctorate from Indian Institute of Science, Bangalore. For the first two and a half decades, he worked in the areas of thermal hydraulic analysis of reactor core and reactor systems, thermal design of process equipment and process safety and transient analysis of nuclear power plants. His current interests include planning and analysis of issues related to electricity generation, human resource development, technology transfer, extra mural funding and facilitating scientific collaboration between DAE institutions and others at the national and international level. He is currently Director, Strategic Planning Group, DAE as well as Associate Director, Technical Coordination and International Relations Group, BARC. Dr. Grover is a fellow of Indian National Academy of Engineering.

Introduction

Department of Atomic Energy has been working right from its inception for harnessing nuclear science and technology for the progress of the nation based on a well-planned strategy involving simultaneous pursuit of basic research and technology development. This is being done by fostering alliance between scientists pursuing basic research and scientists engaged in technology development within the department as well as by instituting schemes for encouraging alliance with other agencies in the country. Simultaneously, the department has pursued human resource development based on alliances of a different kind. In the Training School at Trombay, scientists and engineers, in addition to their regular assignments in the department, teach nuclear science and engineering to orient the newly recruited young graduates before they are absorbed in the department. The advantages of involving practising scientists and engineers in human resource development have been extensively talked about and we have been following this approach for more than four decades. In addition to this internal alliance, the department pursues several programmes in cooperation with the university system in the country, which aims at the development of human

resource as well as R&D activity. All these alliances have contributed towards implementation of the programmes of the department. This article provides a summary of how the policy of creating alliances has led to successes not only for the department, but also developing a hi-tech base in the country.

Early History and Evolution of the Organisation

Homi Jehangir Bhabha formulated the basic strategy for the development of nuclear energy programme in the country at a time when India possessed hardly any infrastructure to nurture hi-tech activity. The first prime minister of India, Jawahar Lal Nehru, helped Bhabha lay the foundations of the atomic energy programme with self-reliance as its motto. Accordingly, Atomic Energy Establishment Trombay (AEET), was progressively set up. This establishment, consists of research reactors and other facilities for research and technology development. AEET was renamed as Bhabha Atomic Research Centre (BARC) after India tragically lost Bhabha in an air crash in 1966 and it has progressively grown into a large R&D establishment.

While setting up various other institutions, the Department has ensured that an organic linkage between all the institutions is maintained, and

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research and development lead to deployment of technologies. To achieve this objective, the DAE, besides establishing research centres, has also set up closely linked industrial units. The resulting synergy between research, technology development and industrial application has benefited all the agencies involved. As a result of all these efforts, India is self-reliant in all aspects of nuclear fuel cycle, starting with prospecting and mining of uranium to the back-end of the fuel cycle, which involves reprocessing of the spent fuel and nuclear waste management. Today, in India the nuclear power reactors are built and operated by the Nuclear Power Corporation of India Ltd. (NPCIL). The Atomic Minerals Directorate of Exploration and Research (AMD) is engaged in prospecting of uranium. The Uranium Corporation of India Ltd. (UCIL) mines uranium. The Heavy Water Board (HWB) produces heavy water and the Nuclear Fuel Complex (NFC) fabricates fuel and structural materials. Most of the R&D work, which led to the setting up of these industrial units, was initiated and pursued at BARC, Trombay. Some of the activities have now been taken over by other research centers: Indira Gandhi Centre for Atomic Research (IGCAR) at Kalpakkam for fast reactors, Centre for Advanced Technology

(CAT) at Indore for accelerators and lasers, and Variable Energy Cyclotron Centre (VECC) at Calcutta for accelerators. Radiation and isotope technologies developed in the R&D Centres are canalized for deployment through Board of Radiation and Isotope Technology (BRIT).

For the development of nuclear power, India is pursuing a three stage nuclear power programme which has been formulated to provide a long term energy security to the country based on indigenous nuclear fuel resources [1]. The programme envisages a closed fuel cycle involving reprocessing of the spent fuel to separate the fissile material for recycling. The first stage comprising of setting up of Pressurised Heavy Water Reactors (PHWRs) and associated fuel cycle facilities is already in the industrial domain. The second stage envisages setting up of Fast Breeder Reactors (FBRs) backed by reprocessing plants and plutonium-based fuel fabrication plants. The third stage will be based on the thorium-uranium-233 cycle. Ongoing implementation of the three-stage programme formulated in mid fifties, demonstrates the technology management acumen of the pioneers of the atomic energy programme in India. Table 1 gives a summary of nuclear power programme.

TABLE 1. Nuclear Power Plants – Present Status and Future Plans

Plants under operation	2720 MWe
14 reactors at 6 sites viz., Tarapur, Rawatbhata, Kalpakkam Narora, Kakrapar and Kaiga	
Plants under construction	3960 MWe
2x540 PHWR at Tarapur 2x220 PHWR at Kaiga 2x220 PHWR at Rawatbhata 2x1000 VVER at Kudankulam	
Plants likely to commence in the current financial year	
1x500 PFBR	
Future Plans	
One AHWR having a rating of 300 MWe and a mix of 500 MWe FBRs, 680 MWe PHWRs and 1000 MWe LWRs so as to reach a total of about 20,000 MWe by the year 2020.	

Human Resource Development

Human resource development has been accorded a very high priority in the department. In the initial stages, it was necessary to set up a mechanism to provide training in nuclear science and engineering. It was based on the realization that programmes of higher education, because of their focus on specialization, have to be linked to employment. Therefore, for recruitment to the DAE, a methodology based on the principle of 'hire and train' was devised and is still being followed [2]. Young graduates are hired and given an orientation course in nuclear science and engineering at BARC Training School. This programme has been in vogue since 1957. As indicated earlier, the faculty for this training school is drawn from amongst the scientists and engineers working in DAE. Practising scientists and engineers, working as adjunct faculty, provide an excellent exposure of the subject to the young trainees. An engineer, working on the design of equipment for a nuclear power plant, is best qualified to teach engineering design to the trainees. Similarly, a physicist engaged in reactor physics calculations can convey the intricacies of reactor physics theory to the trainees.

Besides one-year orientation course, we started another scheme in the Training School in 1992. We have been recruiting engineers with masters qualification in engineering and give them a short orientation course of one semester. From this year, we have started DAE Graduate Fellowship Scheme (DGFS). Students, who have joined masters programme in engineering at select institutes¹, are eligible to apply for this scheme in the beginning of the programme and if selected, they are paid a higher stipend and take up electives and project work in an area of interest to DAE. In the first year itself, 38 students have joined this programme and it means that 38 projects of one-year duration will be carried out at the select institutes under the joint guidance of Institute faculty and DAE scientists. This alliance would create long term bonding, between DAE and the educational institutes.

¹To implement this scheme, agreements have been signed with the Indian Institutes of Technology (IIT) at Roorkee, Delhi, Kanpur, Kharagpur, Mumbai and Chennai.

Alliance with the University System

DAE interacts with the university in several ways.

- DAE provides full financial support to seven grant-in-aid institutions: Tata Institute of Fundamental Research (TIFR), Mumbai; Saha Institute of Nuclear Physics (SINP), Kolkata; Institute of Physics (IOP), Bhubaneswar; Institute for Plasma Research (IPR), Gandhinagar; Institute of Mathematical Sciences (IMSc), Chennai; Harish-Chandra Research Institute (HRI), Allahabad; and Tata Memorial Centre (TMC), Mumbai. These institutes are engaged in front-line research in their respective areas and have continuous interaction with the DAE.
- DAE has several large facilities for research such as research reactors at Trombay, Variable Energy Cyclotron at Kolkata, and Synchrotron Radiation Source Indus-1 at Indore. DAE makes these large research facilities available to the faculty from universities under the auspices of Inter-University Consortium of DAE Facilities (IUC-DAEF). This came into existence with the signing of an agreement in 1989 between DAE and University Grants Commission (UGC).
- DAE funds sponsored research through Board of Research in Nuclear Sciences (BRNS). BRNS attempts to fund collaborative projects, where a part of the work is done in a DAE institution and a part in an educational institution. This again is an attempt to create alliance between DAE institutions and the university system. It will be worthwhile to mention here that the BRNS is the oldest funding agency in the country and was set up as Atomic Energy Committee in 1945 with Bhabha as its first Chairman. Annex 1 gives details of BRNS.
- All R&D centers of DAE establish direct links with the university system; type of linkage, of course, depends on the end objective. To cite an

example, BARC and Pune University have an agreement under which 12 doctoral students are admitted every year in the disciplines of Physics, Chemistry and Biology. These students have two supervisors, one from BARC and the other from the university. To cite an altogether different example, BARC has an agreement with IIT, Bombay, under which research work in the area of thermal hydraulics for the Advanced Heavy Water Reactor is being developed by BARC, is being done at IIT.

- R&D centers of DAE have been recognized as centers of research leading to post-graduate qualification by the universities. Employees of DAE as well as research scholars register for research degrees.
- DAE Graduate Fellowship Scheme for IITs has been launched from this academic year and is already explained in the previous section.

In addition to the foregoing, BARC has an altogether different kind of linkage with the agricultural universities. Genetic mutation of crop plants resulting in improved yield, better characteristics or disease resistance is a continuous endeavour of scientists at BARC. Radiation induced mutations, in contrast to spontaneous variations, enhance the range of variability, from which plant breeders can select and combine desired characteristics to produce better crop plants. Using induced mutations and cross breeding, 23 crop varieties have so far been developed and released for commercial cultivation. Among them are 9 groundnut, 10 pulses and 2 mustard varieties and one variety each of jute and rice. These varieties have been developed in collaboration with agricultural universities in the country and have been named accordingly. For example, one of the groundnut varieties is named as TAG-24. The abbreviation TAG stands for Trombay Akola Groundnut. Trombay represents BARC; Akola represents the agricultural university at Akola.

Alliance with the National Laboratories and Other Government Departments

Simultaneous with the university system, we also interact with the national laboratories and other government departments. This interaction benefits

both sides; DAE benefits from the expertise of other national laboratories in the country and other laboratories and departments benefit from the expertise available in the research centers of DAE. To derive benefits from other laboratories in the country, DAE provides funding for research in areas of interest through BRNS. Examples include development of industrial gas tubes by CEERI, Pilani, setting up of a seismic test facility at SERC, Chennai, setting up of a facility to test equipment under high temperature and pressure environment simulating certain accident conditions at ERDA, Vadodara and several others. Examples of benefits to other agencies include interaction of BARC with the Department of Ocean Development for developing a processing route for separation of nickel and cobalt from the leach liquor of polymetallic nodules mined from seabed. Based on the technology provided by BARC, a pilot plant has been set up at Hindustan Zinc Limited, Udaipur and is undergoing trial runs. BARC has been working on the development of shape memory alloys and these have found application in Light Combat Aircraft. (For more examples, see Ref. [3]).

Alliance with Industry and Technology Management in the Department

As mentioned earlier, research and technology development have to be pursued together with the ultimate aim of deploying the results for societal development. The DAE pursued several mechanisms to achieve this objective [3]. Some of these were planned, while some have happened spontaneously. We may classify them as follows.

1. In-house technology transfer.
2. In-house technology deployment.
3. Development of indigenous vendors and technology spill over.
4. Technology transfer to outside agencies,
 - Technologies developed as per mandate, and
 - Technology spin-offs.
5. Technology diffusion.

Setting up of industrial units and public sector units under the DAE are the examples of in-house technology transfer. Setting up of research reactors,

fuel reprocessing facilities and waste management facilities are the examples of in-house technology deployment. For both these categories, Indian industry was involved in a big way and in the process of vendor development, the engineers of the DAE interacted with the engineers of Indian industry resulting in upgrading the skills of the industry. This skill upgradation had a spillover effect, whereby the expertise gained by the industry was used by them for other sectors of the economy.

In addition, R&D centers of DAE have transferred several spin-off technologies to the industry (see Annex 2 for list of technologies transferred). Consultancy in hi-tech areas is provided regularly by the institutions of DAE (see Annex 3 for list of consultancy services offered). Two areas are particularly noteworthy: non-destructive testing and application of isotope and radiation technology to industry. Simultaneous with all above, technology diffusion has been continuously taking place from DAE activities. BARC developed techniques for radiography and conducted courses for training personnel in the use of these techniques including safety in handling of radioisotopes. Till date about 6000 persons have been trained and are working in the industry in India and Gulf countries, where certification by BARC is recognised. BARC conducts courses in the area of nuclear medicine and nearly 120 nuclear medicine centres and 650 radioimmunoassay centers, manned by personnel trained by BARC, are working in the country.

Concluding Remarks

The DAE has successfully exploited nuclear technology for national development and has also

acted as a catalyst for the growth of hi-tech in India. Every possible mechanism to ensure that technologies developed by the research centers are deployed has been utilized. As a result of these efforts, the first stage of the nuclear power programme is in commercial domain. Many applications of radiation technologies have been developed and conscientious efforts are being made for their countrywide deployment. Considering that India now has a mature technology base, DAE has formulated a programme for increasing the nuclear installed capacity to about 20,000 MWe by the year 2020, the present capacity being 2740 MWe.

Several factors have contributed to this success story. Some of the important factors have been cited here and include emphasis on human resource development, alliance of R&D centers and industrial units within DAE, alliance with the university system, the national laboratory system and the Indian industry.

References

1. H.J. Bhabha, "General Plan for Atomic Energy Development in India", Conference on Development of Atomic Energy for Peaceful Purposes in India, Nov, New Delhi, (1954) pp 7-21.
2. R.B. Grover et al., "Higher Technological Education", INAE National Seminar on Engineering Education for the 21st Century, Madras, January (1997).
3. R.B. Grover, "Technology Management by the Department of Atomic Energy", INAE National Seminar on Technology Management, Pune, October 12-13 (2001).

Annex – 1

Board of Research in Nuclear Sciences

The Department of Atomic Energy (DAE) supports extramural research and development activities through the Board of Research in Nuclear Science (BRNS). The BRNS support Universities, Institutes of higher learning and National Laboratories in the fields relevant to the mandate of DAE. The Board is chaired by an eminent scientist/engineer and has senior scientists/engineers from within the DAE and outside as members.

Four Advisory Committees assist the Board in the discharge of its duties. Each Advisory Committee is chaired by a member of the Board and is composed of very senior scientists from various DAE units and with an experienced scientist as its Member Secretary. In brief these Committees and their priority theme areas are:

Advanced Technologies Committee (ATC)

Advanced technologies related to nuclear science, nuclear fusion, accelerators, lasers, cryogenics, computers and information technology, artificial intelligence and robotics, automation and controls, sensors, new materials, photonics and other strategic technologies of vital importance to the department.

Basic Sciences Committee (BSC)

Basic and applied research in radiochemistry, actinide chemistry, radiation and photo-chemistry, laser induced chemical reactions, unique catalysts, nano materials, cell and molecular biology, mutagenesis, radiation biology, condensed matter physics, laser and plasma physics, nuclear and particle physics, spectroscopy, etc.

Nuclear Reactors and Fuel Cycle Committee (NRFC)

Structural/civil/mechanical/metallurgical/chemical engineering, material development, heat transfer, fluid flow, water chemistry, nuclear fuels, nuclear safety, environmental impact of nuclear establishments etc.

Radiation Technology and Applications Committee (RTAC)

Radiopharmaceuticals, radio-assays, radioisotopes, radiation technologies, tracer techniques, hydrology etc.

To execute the overall functioning of BRNS Secretariat, well qualified senior scientific officers from various scientific disciplines work as Programme Officers, who may be contacted for details about activities of BRNS. Various schemes of BRNS are described here in brief.

Support to R&D Projects

BRNS supports high quality research & development on advanced concepts of relevance to DAE. The support extended is primarily based on the R&D facilities available in the investigator's institution. BRNS funds are made available to the faculty members of the universities, research/educational institutions of higher learning and national laboratories. Emphasis is laid on collaborative programmes between DAE scientists and scientific community outside DAE family.

Special Projects

In addition to the normal projects submitted by the principal investigators for financial support, BRNS also considers some intensively funded schemes of importance to DAE as well as to create major centres at selected places to develop expertise in a particular area of science and technology. These proposals are funded after critical evaluation and wherever necessary BRNS constitutes separate sub-committees with experts drawn from both within and outside DAE for evaluation and follow-up.

Research Associateships

With an objective of encouraging talented science and engineering doctorates to pursue a career in scientific research in the field of atomic energy, BRNS instituted a scheme named after the

renowned physicist, Dr. K.S. Krishnan on the occasion of his Birth Centenary. Under this scheme Research Associates are inducted every year for a 2-year Associateship with the possibility of getting absorbed in one of the four R&D organisations of the DAE (BARC, CAT, VECC or IGCAR) against regular vacancies. The appointment is based on their performance and evaluation by the concerned DAE unit.

DAE – Homi Bhabha Chairs and DAE-BRNS Senior Scientist Scheme

These positions are instituted in recognition of sustained record of excellence and creative

contribution to research and/or teaching in the areas of interest to DAE.

In addition BRNS also funds symposia and conferences, administers a visiting scientist scheme and provides foreign travel assistance to the investigators of BRNS funded projects. For details, visit www.barc.ernet.in or contact the following programme officers.

1. Dr. P.P. Chandrachoodan (for ATC & NRFC)
2. Dr. G.R. Relan (for BSC)
3. Dr. S. Trehan (for RTAC, Fellowships/ Associateships)

Email: brns@magnum.barc.ernet.in

Annex 2

List of Spin-Off Technologies from BARC for Transfer to Industry

I. New Technologies Available for Transfer

A. Environment and Health

1. Direct Reading Dosimeter (QF- DRD)
2. Hospital Information Management System Software. (HIMS)

B. Electronics, Electrical and Mechanical

1. Potentiostat/ Galvanostat
2. Controlled-Potential Coulometer
3. Canned Motors
4. Servo Power Amplifier for AC Servomotor
5. 20-kV, 10-80 kJ Energy Storage Capacitor Bank
6. Glass to Metal Seals
7. Intelligent Braille System
8. Electron Beam Welding Machine
9. High and Ultra High Vacuum Bellows Sealed Valves
10. Motion Feed Throughs for Ultra High Vacuum
11. Bayard Alpert Vacuum Gauge

12. Ionisation Gauge Controller

13. Auto TLD Badge Reader (Model TLDBR 7B)
14. Spectroscopy Amplifier (A225)
15. Electrochemical System
16. Digital Pocket Radiation Dosemeter (DIGIDOSE)

C. Chemical and Metallurgy

1. Ship borne Desalination Plant/ Fresh Water Generator
2. Improved Method for Fluoride Removal from Aqueous Effluent
3. Yttrium Vanadate Phosphor
4. Hydrogel dressings for burn/ injury treatment
5. On-line domestic water purifier based on ultra filtration polysulfone membrane
6. Production of optical quality electro less nickel (EN) coating on copper substrate.

II. Technologies Already Transferred

These have been transferred on non-exclusive basis. Technologies marked with * were developed and transferred long back.

A. Environment and Health

1. Bilirubin Strips
2. Infra-red Carbon Monoxide Analyser*
3. Carbon Monoxide Monitor (catalytic)*
4. Nitric Oxide Monitor*
5. Sulphur Dioxide Monitor*
6. Ozone Generator*
7. NO_x and NH₃ to NO Converter*
8. Ozone Monitor*
9. Air Quality Data Processor*
10. TLD Badge Reader
11. Special Cylindrical Particulate Filter*
12. Microprocessor Based Electromyograph*
13. Particulate Respirator Filter Canister*
14. TLD Badge for Personnel Monitoring
15. Impedance Plethysmograph
16. Accreditation of Personnel Monitoring Laboratory
17. Impedance Cardio Vasograph
18. Cardiac Output Monitor
19. Portable Radiation Monitors (package of the following 3)
 - Digital Contamination Monitor (DIGICON)
 - Industrial Radiation Monitor (INDRAM)
 - Radiation Monitor (RADMON)
20. Radiation Dosimeters (package of the following 4)
 - Secondary Standard Dosimeter SSD-590
 - Clinical Dosimeter
 - Universal Dosimeter
 - Beam Therapy Dosimeter BTM-2A
21. Vibro-thermal Disinfector(VTD).

B. Electronics, Electrical and Mechanical

1. Space Quality Silicon Solar Cells

2. Microprocessor Based PABX/PAX*
3. Automatic Fraction Collector*
4. X-Ray Generator Power Supply*
5. Electromechanical Actuator*
6. Surface Area Measuring Apparatus*
7. Image Analysis System*
8. Drag Cup Induction AC Servo Motor*
9. Pneumatic Pick and Place Robot*
10. High Security Electronic Lock*
11. Eccentric Collet Chuck*
12. Technique for Tee/branch Formation in Tubular Products*
13. Laser Tube Power Supply for Low Power He-Ne Lasers
14. Distributed CCTV Control System
15. Hospital Information Management System (Software)
16. 8 K MCA PC Add on Card PCA-95
17. Front Office Postal Machine*
18. Foldable Solar Dryer
19. Triode Sputter Ion Pumps
20. Lascan Dia Gauge
21. Master Slave Servo Manipulator
22. Particle Size Classifier
23. Mini-Micro Stepping Control Drive & Associated Drive Software with Algorithm for Stepper- Motor
24. Video Frame Buffer PC-add-on Card
25. PC add on Card for 20 million Samples per Record (ANUDAQ - 20)
26. 100 MSPS Transient/ Waveform Digitizer
27. Spectrum Stabilising PC MCA Card (PHAST2)
28. Laser based Digital Data Communication System
29. On-line Set Point Servo System (OLSPSS)

C. Chemical and Metallurgy

1. Low Carbon Ferroalloys

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|--|--|
| 2. Osmotic Dehydration of Fruits | 16. Preparation of CaSO ₄ : Dy TLD Phosphor* |
| 3. Carbon Blocks / Bricks Refractory (Patent)* | 17. Process for the Enzymatic Production of Invert Sugar Syrup |
| 4. Production of Elemental Phosphorus* | 18. Process for production of Pressure Sensitive Adhesives* |
| 5. Enrichment of Nitrogen-15* | 19. A Bio-pesticide based on Bacillus Thuringiensis |
| 6. Production of Sulphur Hexafluoride | 20. Recovery of Tungsten, cobalt, Tantalum, Niobium and Titanium from Hard Metal Scrap |
| 7. Advanced Pressure Electrolyser for production of H ₂ /O ₂ | 21. Diethyl hexyl Phosphoric acid (D2EHPA) |
| 8. Reverse Osmosis Plant (Tubular Module)* | 22. Porous polysulfone diaphragm as separator in electrochemical process. |
| 9. Boron Carbide B ₄ C | |
| 10. Reverse Osmosis Plant (Plate Module) | D. Radio Isotope Applications |
| 11. Zirconium Oxide/ Oxychloride | 1. Gamma Radiography Equipment* |
| 12. Field kit for Identification of Molybdenum in Steel* | 2. Technique of Mercury Inventory in Electrolytic cell |
| 13. Field Kit for Identification of Nickel & Chromium in Steel* | 3. Gamma Switch* |
| 14. Aluminium Zirconium Master Alloy | 4. Rig testing of Combined Particulate and Iodine Filters |
| 15. Process for Corrosion Resistant Oxide Coating in Zircaloy-2 | |

Annex - 3

Consultancy Services from DAE

- | | |
|---|--|
| 1. Isotope Applications in Industry | • Modal analysis of structures for qualifying the analytical model |
| • Gamma scanning of process towers | • Dynamic response measurement |
| • Leak detection of buried pipelines, heat exchangers using radioactive tracers | • Design qualification through modal studies |
| • Location of leakage in pipelines and other systems using radioactive sources | • Trouble shooting of structures like piping and rotating machinery |
| 2. Radiography Testing & other NDT Techniques | • Piping qualification as per ASME operation & maintenance codes |
| • Special and unusual isotope radiography | • Diagnostics of structures and machinery by mechanical signature analysis |
| • Eddy current imaging | 5. Analytical Chemistry Services for applications to |
| • In situ metallography | • Geological Materials |
| • Acoustic emission | • Metals & Alloys |
| • Digital signal analysis | • Environmental Materials |
| • Laser holography and interferometry | • Forensic Science |
| 3. Electron Beam Services | |
| 4. Vibration Assessment and Diagnostics | |

- Archaeology
- 6. Chemical Engineering
- Process evaluation and review
- Integrated energy management, process retrofitting and process re-engineering
- Commissioning assistance and safety assessment
- 7. Structural Analysis and Design
- 8. Coating technology
- 9. Qualification approval, ageing & failure analysis
- 10. Metrology & special inspection techniques
- 11. Computer aided manufacturing
- 12. Desalination techniques
- 13. Vacuum engineering
- 14. Advanced process instrumentation and controls
- 15. Process equipment design
- 16. Robotics & remote handling
- 17. Heat transfer and fluid flow
- 18. Tissue culture and bio-reactors
- 19. Digital signal processing techniques & applications
- 20. Parallel processing & virtual reality applications.
- 21. Mineral technologies

NAA and other Radioanalytical Techniques : Trace Element Determination



Prof. Amar Nath Garg obtained his M.Sc. from Agra University in 1965 and Ph.D. from Indian Institute of Technology, Kanpur in 1970. During 1974 to 1976 he worked on the analysis of lunar rocks with Prof. William D. Ehmann as post doctoral fellow and NASA co-investigator. His research activities include Mossbauer spectroscopic studies of structure and bonding in iron complexes, radiation chemistry of inorganic nitrates and aqueous systems, trace element analysis for biomedical, nutritional and environmental studies by neutron activation. He guided 14 Ph.D. and an equal number of M.Phil students. After serving Udaipur University as lecturer in chemistry (1971-79), he joined Nagpur University as reader in chemistry where he established a radiochemical laboratory. Presently he is Professor in chemistry at the Indian Institute of Technology, Roorkee. Besides completing several BRNS, CSIR and UGC research projects, he also participated in two Coordinated Research Projects of IAEA. He holds a Japanese patent on multitracers and was chemical abstractor to Chemical Abstracts Service, USA for 12 years. Prof. Garg is a member of several professional bodies. He is currently Vice-President of Indian Association of Nuclear Chemists and Allied Scientists.

During mid eighties when I was attending a symposium in the Department of Chemistry, University of Mysore where Dr. K.N. Rao then Head, Chemistry Division, BARC was an invited speaker, mentioned about the availability of financial assistance from the DAE. Since I had experience of working with Prof. P.S. Goel at IIT Kanpur and Prof. William D. Ehmann at the University of Kentucky (USA), active workers in the field of NAA, I submitted a proposal for supporting my NAA work on trace element determination in geological and related samples. I was asked to resubmit it, interact with Dr. M. Sankardas in Analytical Chemistry Division and use his facilities. Thus, my first project started in November 1981 and that was the beginning of my interaction with BRNS. Later Dr. Satya Prakash introduced me to the facilities in Radiochemistry Division, which proved to be a boon for my research career. During subsequent years I had four more projects including a DAE research fellow till I left Nagpur University in September 1996. Besides, I also had the privilege of having two Coordinated Research Projects (CRPs) supported by the International Atomic Energy

Agency (IAEA), Vienna. After joining my present assignment at Roorkee now Indian Institute of Technology I decided to establish high resolution gamma ray spectrometry facility and this resulted in my present BRNS project on the analysis of medicinal herbs and herbal preparations which started in December 2000.

Neutron activation analysis (NAA), discovered by George de Von Hevesy in 1936, is essentially a nondestructive nuclear analytical method ideal for the determination of major, minor and trace elements in all kinds of matrices such as geological, biological, environmental, industrial and forensic [1,2]. Since seventies onwards, it has opened up the field of trace elements in biological processes leading to the recognition of many elements as essential even though these were toxic at higher concentrations. The method of NAA involves irradiation of a sample with neutrons in a nuclear reactor followed by assay of γ -activity of radionuclides so formed and calculating the concentration of element [3]. During last two decades, we have worked extensively on trace

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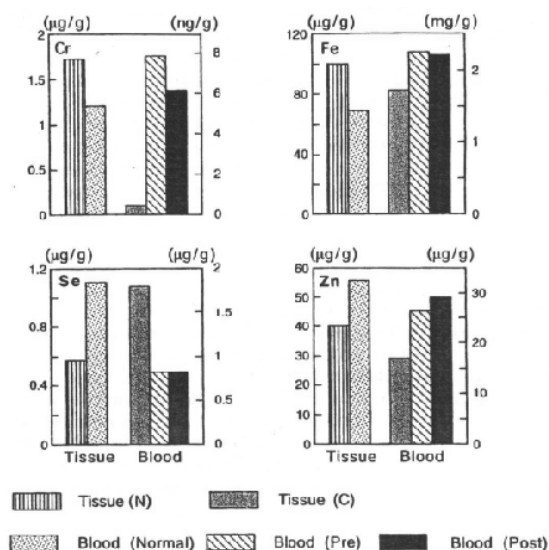


Fig. 1 Comparison of elemental contents in tissue and blood samples of breast cancer patients with those of controls

element determination in geological, environmental, nutritional, biomedical and bioenvironmental studies by NAA and radioanalytical methods including isotope dilution analysis (IDA). A variety of samples were analysed e.g. respirable dust particulates from mica mines and factory, vegetarian diets and its constituents, breast cancer tissue of different histopathological stages including blood of cancerous patients, milk powder and milk of different origins, hair samples of industrial workers, fish from three coastal areas, cigarette tobacco including its smoke and ash, ambient and fugitive air particulates from cement factories and a thermal power station, ambient air samples from residential, commercial and industrial zones of six metropolitan cities. In the following lines I shall attempt to briefly describe some of our work.

Analysis of Breast Cancer Tissue and Blood

Our collaborative studies with Prof. V. Sagdeo, at the Government Medical College, Nagpur have resulted into a very useful correlation of breast cancer with Se deficiency and its dietary intake [4]. In a comparative study of minor and trace elements in breast cancer and normal tissue from 30 patients of four histopathological stages, differential patterns of

enhancement and depletion were observed. Incidentally Se is enhanced by ~95% in cancerous tissue followed by K, P, Cu and Zn whereas Cr, Mn and Fe are depleted. In order to trace the source of elemental enhancements or depletions, blood samples of breast cancer patients in pre and post operation stages were analysed and compared with those of controls [5]. A comparison of elemental contents in tissue and blood samples of the cancer patients is shown in Fig. 1. Lowering of Se (~54%) in blood is correlated with its enhancement in cancerous breast tissue of various clinical stages. Lowering of Se/Zn and Se/Fe ratios in the cancerous tissue and marginal enhancement of Na/K have been correlated with the stage of disease. Further, an attempt has been made to correlate Se levels with the dietary intake and breast cancer risk vis-a-vis American and Japanese woman. According to a formulation proposed by Schrauzer et al.[6], blood Se concentration and per capita Se intake for adults are correlated as

$$Se_{\text{intake}}(\mu\text{g/d}) = 1104 Se_{\text{blood}}(\mu\text{g/mL}) - 35$$

It has been suggested that lowering of per capita dietary Se intake of 250 to 125 µg/d could cause an approximately four to five fold increase in breast cancer risk. Using this formulation Se intake of the population group under study is found to be approximately 340 and 120 µg/d for controls and breast cancer patients respectively. Therefore, low Se dietary intake is associated with higher risk of breast cancer [5].

Analysis of Indian Diet and Dietary Constituents

During last few decades, there has been increasing awareness about essentiality of many trace elements including Fe, Zn, Mn, Co, Cu and Se. In order to maintain functional and structural integrity of the tissue and safeguard its growth, health and fertility characteristics, concentration and functional form of trace elements must be strictly maintained within narrow limits [7]. In an attempt to determine trace element intake through Indian diet we had prepared two typical vegetarian diets in raw form with formulation as per recommendations of the National Institute of Nutrition (NIN), Hyderabad. On the basis of analysis of such diets daily dietary intake (DDI) of Fe, Zn, Cu and Mn were calculated and compared with WHO and American

TABLE 1. Comparison of DDI for adult diet with WHO and American RDAs

Element	Concentration (µg/g)	Total intake (mg/day)	RDA (WHO) (mg/day)	Am. Med. Asso. (mg/day)	National Res. Council (mg/day)
Iron	44.9	23.8	20-30	18	15
Zinc	17.2	9.10	5.5-11	15	15
Manganese	7.6	4.02	2-3	-	2-5
Copper	3.5	1.85	2	2	1.5-3

RDAs as given in Table 1. It is observed that typical balanced vegetarian diet for an adult in the middle income group has sufficient amounts of Fe, Mn, and Cu when compared with RDAs of various agencies [8]. However, iron content in our diet is somewhat higher whereas zinc content is comparatively lower than RDAs. In order to see the effect of cooking we have further analysed total diet supplied to an individual in Medical College Hospital, Nagpur. It is vegetarian and as per recommendations of dietician. Three diet samples were collected over a period of 6 months at different intervals and analysed for 20 elements. It was observed that some elements were in uniform concentration range whereas others were found to vary in a wide range and attributed to different vegetables and wheat/rice variety. From the mean elemental contents, DDI of selected elements were calculated and compared with those from other countries. Critical comparison of mean DDI for most of the elements are in a comparable range [9].

Analysis of Water

Water is vital to life and its elemental composition is important to life processes as it provides all the essential nutrients to living organisms. Water samples from different sources (reservoir, well, borewell, sewage tank, river and rain) in and around Nagpur city including doubly distilled and a sea water from Mumbai were analysed for 27 elements (Ag, Au, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Ga, Hg, Hf, K, La, Mn, Na, Sb, Sc, Sr, Th, P, Ta, Tb, Zn and Zr) after preconcentration by evaporation [10]. In spite of wide variations in elemental concentrations, most elemental contents in drinking water were within ISI/WHO limits. However, sea water from Mumbai showed higher concentrations for pollutant elements such as Ba, Cr, Fe, Hg and Sb

but for doubly distilled and rain water, elemental contents were very low[11].

NAA using $^{241}\text{Am-Be}$ Source

Chemistry Department of Nagpur University acquired a $5\text{Ci } ^{241}\text{Am-Be}$ neutron source emitting $\sim 10^5 \text{ n cm}^{-2} \text{ s}^{-1}$. We had employed it for the analysis of major constituents of bauxite, pyrolusite and chalcophyrite ores and alloys. Al, Si, Fe, Mn, and Cu were determined using the nuclear reactions $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$, $^{28}\text{Si}(n,p)^{28}\text{Al}$, $^{56}\text{Fe}(n,p)^{56}\text{Mn}$, $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$, and $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$ respectively by employing thermal and fast neutrons [12,13]. A cyclic neutron activation analysis method (CNAA) was developed and used in the determination of Al. It has been shown that chemical and spectrophotometric methods were tedious, time consuming and not economical, whereas NAA methods could provide fast and accurate data without ever dissolving the sample. The methods had the potentiality of being used for on-line analysis of ores, minerals and alloys. This work was carried out primarily as a part of an UGC project.

Determination of P in Biological Samples

In general P can not be determined by NAA because the product nuclide $^{32}\text{P}(t_{1/2}=14.3\text{d})$ is a pure β -emitter. We have developed a method, which uses thermal neutron irradiation for 5-10 h in a reactor followed by β -counting on an end window gas flow proportional counter using 27 mg/cm^2 Al filter after a delay of 2-3 weeks [14]. The results for several Standard Reference Materials (SRMs) were within $\pm 10\%$ of the certified values. The method is ideal for the analysis of biological samples such as cereals, vegetables, spices, milk powder and tissue samples where phosphorus content is of the order of a few mg/g.

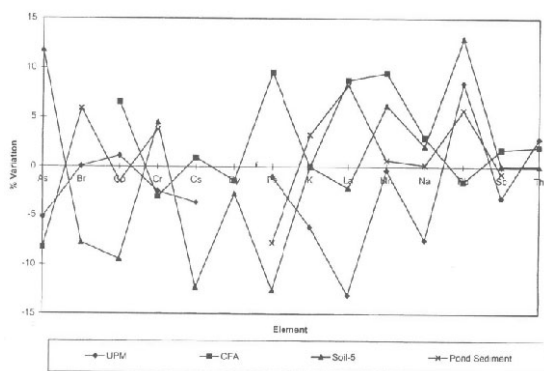


Fig. 2 Comparison of elemental contents in SRMs with their certified values

Validation of Data by k_0 Method

K_0 NAA has been adopted and standardised in Radiochemistry Division, BARC. In order to validate analytical data, k_0 NAA method has been employed and by determining sub-cadmium to epi-cadmium flux ratio for four irradiation sites in APSARA reactor using gold as monostandard. We redetermined the k_0 -factors for 21 elements. This methodology has been applied to obtain multielemental profiles in several environmental SRMs such as Urban Particulate Matter (SRM-1648a), Coal Fly Ash (SRM-1633a), Soil-5 (IAEA), and Pond sediment (NIES, Japan). The measured values were in good agreement with the literature values as evident from Fig. 2. Overall deviations were within $\pm 10\%$ for most elements [15]. Further, elemental concentrations were determined in Ganga river sediments collected from different locations in Kanpur, an industrial city with many tanneries. Elemental data were used to study mobility pattern of Cr and other toxic heavy metals originating from the tanneries along the river flow.

Collaborative Studies with ITRC, Lucknow

In a collaborative study with Industrial Toxicology Research Centre (ITRC), Lucknow respirable mica dust samples from mica mines and a factory in Bihar were analyzed for several elements by INAA and RNAA methods. Both sample types showed the presence of several toxic elements such as Ba, Cr, Cd and Sb in appreciable quantities [16]. When tested in a rat model system over a period of

365 days after intratracheal injection of respirable mica dust, animals exhibited enhanced dust induced pulmonary reaction together with characteristic abscess formation at later periods. Toxic effects of elemental contents could be correlated with chronic pulmonary damage in rats.

In another study of environmental pollution in and around a petroleum refinery complex near Mathura, NAA method was used to assay concentrations of As, Ba, Br, Cl, Co, Cr, Cs, Cu, Fe, Hg, La, Mn, Mo, K, Na, P, Sc, Rb, Se, Sr, W and Zn in the rumen fluid ash samples of buffaloes from its vicinity. Corresponding control samples were collected from Lucknow, 300 km away from the refinery. It was observed that mean elemental concentrations of As, Ba, Br, Cr, Hg and Fe were enhanced whereas those of Na, K, Cl, Cu, Mn and P were depleted in samples from the refinery complex compared to controls [17]. A correlation between two groups of elements has suggested the possibility of a disturbed controlling homeostatic mechanism. It has been concluded that industrial emissions do affect the surrounding vegetation / water and the stock animals which may affect human beings adversely.

Collaborative Studies with NEERI, Nagpur

In order to assess the source of pollutants and the atmosphere quality, several studies were attempted in collaboration with the Air Pollution Control Division of the National Environmental Engineering Research Institute (NEERI), Nagpur. Multielemental profiles of ambient and fugitive dust particulates were studied from two cement factories and Korba thermal power station in central India [18,19]. Significant differences were observed for many toxic elements such as Fe, Co, Br, Mn, Ba, Cr and Cd at different locations. The data have been interpreted in terms of air quality inside the plant and residential colonies of the factory. Furthermore, a comparative study of elemental contents of dust particulates from the plant with environmental standards such as Urban Particulates Matter, Coal Fly Ash and Vehicle Exhaust provide a clue to better understand our atmosphere (20). Also ambient air particulates from residential, commercial and industrial zones of six metropolitan cities (Delhi, Mumbai, Kolkata, Chennai, Cochin, and Nagpur)

TABLE 2. Elemental concentrations in typical medicinal plant leaves

Sample	Cr (µg/g)	Mn (µg/g)	Fe (µg/g)	Co (ng/g)	Cu (µg/g)	Zn (µg/g)	Se (ng/g)
Tuisil <i>O. sanctum</i>	0.79	54.1	72.3	30	12.8	17.9	112
Brahmi <i>C. asiatica</i>	0.53	223	217	309	26.7	53.0	59
Neem <i>A. indica</i>	0.94	53.3	54.8	11	-	27.2	4.6
Shankhpushpi <i>C. decussata</i>	0.35	68.9	261	229	55.2	74.2	645

were analyzed whereby significant differences in elemental contents were observed.

Analysis of Medicinal Herbs and Herbal Preparations

Ayurveda, the traditional medicinal system developed thousands of years ago in the Indian subcontinent also emphasizes the importance of minor and trace elements in human health and disease. Several metallic preparations with organic macromolecules, referred to as bhasmas are widely used for curing a variety of disorders. Numerous plants and derived medications used for treating inflammation and fever, malaria, ulcer, memory loss, reproductive behaviour, cardiac arrest etc. have been analysed. For several medicinal herbs including Tuisil, Neem, Brahmi, Arjun (bark), Ashwagandha, Ginseng, Shatavari, Kanher, Vekhand etc. minor and trace element contents were correlated with their therapeutic properties [21,22]. Typical data for some leaf samples often used in Indian household are listed in Table 2. In my present BRNS project on the analysis of medicinal herbs and herbal preparations, a high resolution gamma ray spectrometry facility has been set up at IIT Roorkee. Several brands of a herbal preparation, Trifala (a mixture of harad, baheda and amla in equal amounts) have been analyzed for Na, K, Mg, Ca, Al, Cl, V, Mn, Br, Cu etc. Overall elemental contents of different brands were found to be similar but these were enriched in several nutrients.

Recently we have analyzed several brands of tea from India and US for Na, K, Mn, Cu and Br after 2 h reactor irradiation. Typical γ -ray spectrum of

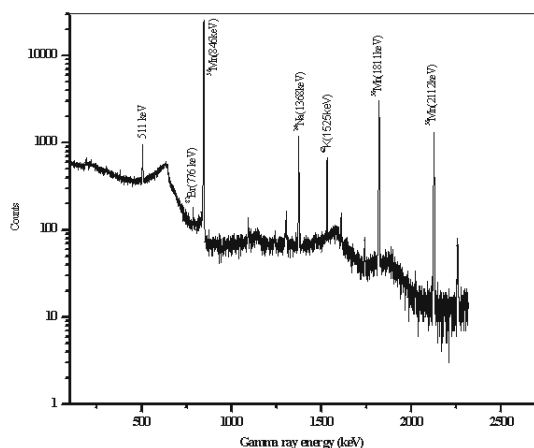


Fig. 3 Gamma ray spectrum of typical tea leaves after 2 h irradiation

irradiated tea leaves sample with identification of radionuclides is shown in Fig. 3. It has been observed that Indian tea is rich in mineral contents compared to US tea though K contents are similar [23]. Tea is a rich source of manganese (500 – 800 µg/g) and tea beverage is useful for supplying this mineral nutrient.

Isotope Dilution Analysis Methods

For many elements such as Cr, Mn, Fe, Co, Zn, Sb, Se and Mo, IDA methods based on solvent extraction have been developed using radiotracers [24]. In this methodology specific reagents were developed and experimental conditions such as pH, choice of solvent, time of equilibration, quantitative nature, chemical and radiometric interferences were studied. In several cases substoichiometric IDA

methods were developed. The methods so developed were employed for the analysis of biological and environmental SRMs and real samples. A substoichiometric IDA method was developed for the determination of iodine in different brands of common salt [25]. It uses ^{131}I tracer and NaI as carrier wherefrom liberated iodine is extracted in CCl_4 . Later AgNO_3 was added in substoichiometric amount for the precipitation of AgI whose activity was counted by scintillation gamma ray spectrometry. The method is specially useful for the determination of iodide in presence of excess of chloride.

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References

1. W.D. Ehmann and D.E. Vance, Radiochemistry and Nuclear Methods of Analysis, John Wiley & Sons, New York, 1991.
2. Z.B. Alfassi, Ed. Chemical Analysis by Nuclear Methods, John Wiley & Sons Ltd., New York, 1994.
3. C. Vandecasteele and C.B. Block, Modern Methods of Trace Element Determination, John Wiley & Sons Ltd, Chichester, 1997.
4. A.N. Garg et al., Biol. Trace Element Res, **46** (1994) 185.
5. V. Singh and A.N. Garg, Biol. Trace Element Res, **64** (1998) 237.
6. G.N. Schrauzer et al., Jpn. J. Cancer Res., **76** (1985) 374.
7. A.S. Prasad, Ed., Essential and Toxic Trace Elements in Human Health and Disease: An Update, Alan R. Liss. Inc., New York, 1993
8. D.L. Samudralwar and A.N. Garg, Fresenius J. Anal. Chem, **348** (1994) 433.
9. V. Singh and A.N. Garg, J. Radioanal. Nucl. Chem., **217** (1997) 139.
10. M.N. Ambulkar et al., Appl. Radiat. Isot. **43** (1992) 1171.
11. M.N. Ambulkar, N.L. Chutke and A.N. Garg, J. Radioanal. Nucl. Chem., **207** (1996) 3.
12. R.J. Batra and A.N. Garg, J. Geol. Soc. India, **32** (1988) 351.
13. R.J. Batra and A.N. Garg, J. Radioanal. Nucl. Chem., **129** (1989) 335.
14. R.G. Weginwar et al., J. Radioanal. Nucl. Chem., **133** (1989) 317
15. V.V.S. Ramakrishna, R.N. Acharya, A.V.R. Reddy and A.N. Garg, Appl. Radiat. Isot, **55** (2001) 595.
16. A.N. Garg, W.K. Wankhade, R.K.S. Dogra and R. Shanker, Sci. Total Environment, **67** (1987) 165.
17. A.N. Garg et al., Appl. Radiat. Isot., **47** (1996) 581.
18. R.G. Weginwar and A.N. Garg, J. Radioanal. Nucl. Chem., **162** (1992) 381.
19. M.N. Ambulkar et al., Sci. Total Environment, **14** (1994) 93.
20. A.N. Garg et al., J. Radioanal. Nucl. Chem., **192** (1995) 307.
21. D.L. Samudralwar and A.N. Garg, Biol. Trace Element Res., **54** (1996) 113.
22. V. Singh and A.N. Garg, Appl. Radiat. Isot. **48** (1997) 97.
23. A. Kumar et al., Communicated
24. A.N. Garg, R.G. Weginwar and N.L. Chutke, Sci. Total Environment, **139/140** (1993) 42
25. V. Singh and A.N. Garg, Analyst, **119** (1994) 1417

Studies on the Role of Organic Acids in Chemical Speciation and Plant Availability of Cadmium using Radiotracers



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Introduction

Agricultural plants represent an important pathway for the movement of potentially toxic trace elements from soils to human beings. Contaminant metals can accumulate in considerable amounts in plant tissues and exceed the level of that are toxic to human and animal systems before they produce visible phytotoxic effects. Not only elevated concentrations of metals, but even low level of

metals which enter the food chain via plant uptake from soil constitute potential health hazards in the long term. Among various toxic metals, cadmium is considered an important toxic metal. Cadmium is implicated with several health problems such as hypertension, bronchitis and itai-itai disease. Cadmium although not an essential element, plant roots take it up from soils in various proportions. Variations in cadmium accumulation in the plants

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are the result of the combination of plant and soil factors that influence metal uptake.

In recent years it is emphasized that consideration of total metal concentration does not provide the real picture of bioaccumulation, since only a fraction of the total metal concentration is available for uptake. It needs information regarding various physical and chemical interactions, which they undergo in natural system. The mobility, bioavailability and toxicity of trace metals depend on their physico-chemical forms. Changes in metal equilibrium in soil solution may occur due to alteration in soil moisture, pH, cation exchange capacity, redox potential and metal complexation by naturally occurring species. The chelated-metal compounds are more soluble than inorganic precipitates and their solubility is related to complexing organic matter present in the soil. Soil rhizosphere interactions play prominent role in the element acquisition by the plant. Among the various root exudates, low molecular weight organic acids (LMWOAs) which are negatively charged anions under a wide range of soil conditions possess tendency to react strongly with metal ions in both soil aqueous and solid phases [1]. Therefore, Metal-Organic acid interactions in soil plant system are considered important for mobilization/solubilization of metals from highly insoluble mineral phases and becomes an area of sustained research.

In continuation of our work on Metal-Organic acid interactions in soil-plant system [2-4], the present paper reviews our work on the effect of various organic acids on the uptake and translocation of root absorbed cadmium by maize, tomato, soybean and wheat plants grown in sand and soil culture. The comparison of uptake pattern of the plants grown in soil and quartz sand (inert matrix) are expected to point out the existence of Metal-Organic acid interactions, modifying the chemical nature of cadmium (chemical speciation) and its subsequent uptake by plants. Electrophoretic assay has been conducted to ascertain the chemical nature of organically bound Cd, which was further quantitatively estimated using the combination of ion exchange resins and radiotracer.

Materials and Methods

Pot experiments (sand and soil cultures) under laboratory conditions were performed on maize, tomato, soybean and wheat plants using standard practices. Treatments comprised a Cd solution [$\text{Cd}(\text{NO}_3)_2$], labelled with $^{115\text{m}}\text{Cd}$ at 5 $\mu\text{g/ml}$ level (sand and soil experiments) with synthetic amendments of organic acids in Cd: organic acid ratio (1:1, 1:20, and 1:100 w/w). The predominant acids released by plants under study as root exudates were considered for the present study as follows. Maize: citric acid, malic acid, aspartic acid, glycine; Tomato: citric acid, oxalic acid, aspartic acid, glutamic acid; Soybean: malonic acid, malic acid, aspartic acid, asparagine; Wheat: oxalic acid, malic acid, glycine, methionine.

Different forms of organically bound Cd were also quantitatively (%) estimated using radiotracer and ion-exchange resins, viz. Dowex-50 (cationic), Dowex-1 (anionic) and Amberlite XAD (neutral).

Results and Discussion

The distribution of cadmium in plant tissues (root, shoot and fruit) indicate that 65-85% of cadmium is retained in roots and only a small part of it, is translocated to the aerial parts. Addition of organic acids to cadmium (1:1, 1:20, 1:100 w/w) resulted in a statistically significant increase in cadmium accumulation in the root and aerial parts of the plant in both sand and soil cultures ($p < 0.05$). It is interesting to note, in general, that addition of organic acids alter the cadmium accumulation from cadmium treatments without effectively changing the cadmium distribution in root and aerial part of the plant. An increase in Cd uptake from Cd treatment with increasing supplementation of organic acids may be ascribed to the tendency of Cd to interact with organic ligands resulting into the formation of organically bound Cd, which is soluble, mobile and therefore becomes plant available. This fact finds support by higher uptake of Cd from Cd-organic acid amendments in the plants grown in sand culture compared to soil. Quartz sand is an inert medium and provides a better site for Cd organic acid complexation facilitating the formation of mobile organically bound Cd. Higher SPT values of Cd with increasing concentration of organic acids, in the plants grown in sand medium compared to soil

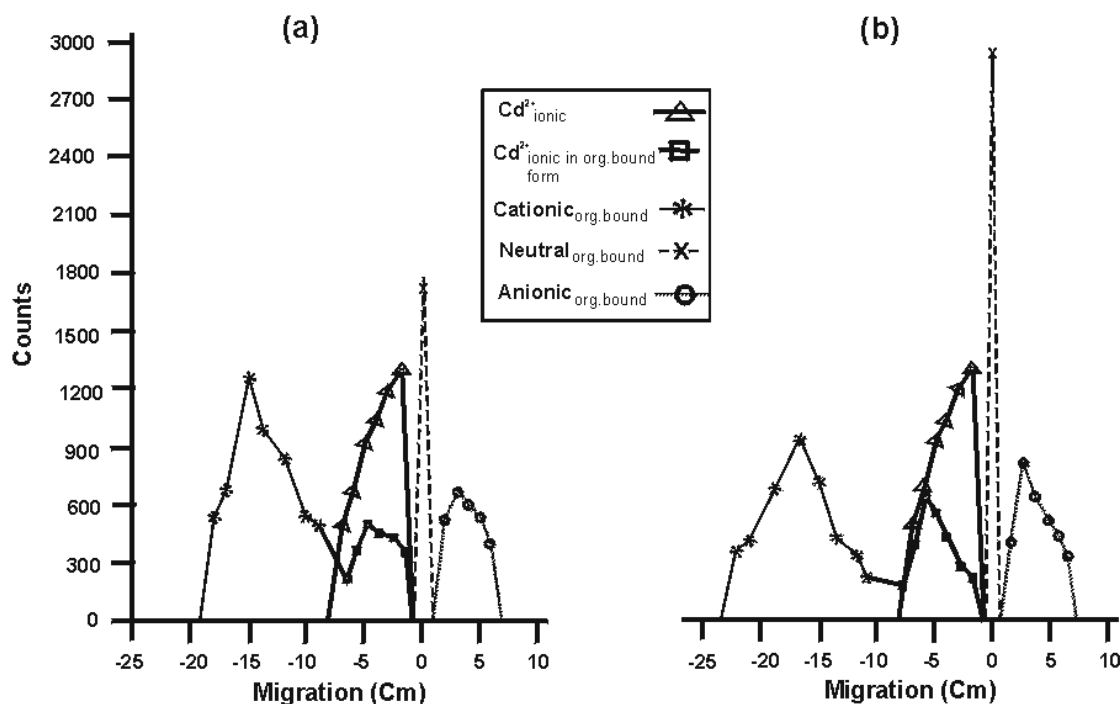


Fig. 1 Plot between counts vs. Migration (cm) on the electrophoretic strip for Cd (a) Malonic acid (b) Asparagine

further, support the observed fact and demonstrate the existence for Cd-organic acid interaction ($p < 0.05$) in soil-plant system.

Cd complexation and resulting uptake are low for amino acids as compared to carboxylic acids. The metal-solubilizing ability of the organic acids is parallel to their metal binding ability, which in turn is correlated with their dissociation constants. The dissociation constants (K_{a1} , K_{a2}) for citric acid (7.0×10^{-4} , 1.6×10^{-4}) oxalic acid (5.9×10^{-2} , 6.4×10^{-2}) malonic acid (1.49×10^{-2} , 2.03×10^{-6}), malic acid (3.9×10^{-4} , 7.8×10^{-6}), aspartic acid (1.3×10^{-4} , 1.5×10^{-10}), glutamic acid (5×10^{-3} , 5.2×10^{-5}) and glycine (1.6×10^{-10}) are in conformity with the order obtained in our experiments.

Poor correlation (non-significant at $p < 0.05$) between the dry matter yield and organic acid additions indicate that the treatments imposed have no toxic effects in spite of higher Cd accumulation in the plants. Organic ligands not only enhance the solubility of the trace metals, but also reduce their toxicity on plants. The free trace metal ions are

reported to be more toxic compared with organically complexed molecules [5].

In order to support our views that plant accumulation of Cd takes place mainly through its organically complexed form, experiments have been conducted to establish the existence, characterization and quantification of organically bound Cd. Electrophoretic nature of Cd^{2+} ions alone and organically bound Cd were recorded separately. A well-defined shift in the peak of Cd^{2+} ions is observed, when it is organically bound. Thus, comparison of the electrophoretic mobility of the above two species (Fig.1) confirms the interaction of Cd^{2+} ions with organic acids resulting into the formation of organically bound form. However, some amount of Cd^{2+} ions remains unreacted and appears as a peak in organically bound solution. These free Cd^{2+} ions in the solution of organically bound Cd were measured by ion selective electrode meant for measuring Cd^{2+} ions. Electrophoretic assay also explains the existence of organically complexed Cd in three forms cationic, anionic and neutral.

Attempts have also been made to estimate all the three forms (cationic, anionic and neutral) of organically bound Cd using different ion exchangers possessing properties of retaining specific form. The three different forms of organically bound Cd are calculated (%) and depicted (Fig. 2). The percentage formation of cationic form of organically bound Cd includes the presence of Cd^{2+} ions (uncomplexed) also. Because, in the present experiment, Dowex-50 a cationic exchanger, could not differentiate between positively charged free Cd^{2+} ions and positively charged organically bound Cd. Therefore, after measuring free Cd^{2+} ions using Cd ion selective electrode and subtracting it from the total cationic species, organically bound Cd cationic form was obtained. Cationic form has found to be predominant in each Cd - complex, formed with carboxylic and amino acids. Dupont et al. [6] studied the mechanistic pathway of the Cd enrichment in plants and found that Cd is probably translocated in the cationic form. Comparative studies of the complexation potential of carboxylic acids and amino acids highlight the affinity of the organic acids under study to form organically bound Cd as follows:

Neutral and Anionic: Asparagine > Methionine > Malic acid > Malonic acid

Cationic: Malonic acid > Malic acid > Methionine > Asparagine

Conclusion

On the basis of our pot culture (sand and soil) experiments, we support the school of thoughts highlighting complexation of Cd as a major contributor for its accumulation in the plants. Organic acids released as root exudates might be expected to have similar effect on rhizosphere soil as observed in the case of synthetic amendments of organic acids. The significant finding that phytochelation of Cd results into its solubilization/mobilization adds an important dimension to the mechanistic strategies of plant enrichment of the metals. The work also explains the inherent capability of the combination of the technique like electrophoresis, radiotracer and ion exchange chromatography providing the knowledge

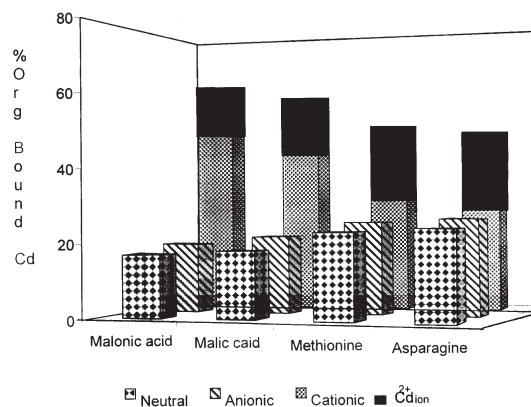


Fig. 2 % formation of organically bound Cd with malonic acid, malic acid, methionine and asparagine.

of various forms (Chemical Speciation) and their reflection on uptake (Plant Accumulation).

Acknowledgement

The authors are grateful to Prof. S.S. Bhojwani, Director, Dayalbagh Educational Institute, Agra for providing necessary facilities. Financial support given by Board of Studies in Nuclear Science (BRNS), Department of Atomic Energy (DAE) is gratefully acknowledged. Thanks are due to Project Director, Nuclear Research Laboratory, Indian Agricultural Research Institute, New Delhi for help in getting soil sample analysed.

References

1. I. Lamy, S. Bourgeois and A. Bermond, J. Environ. Qual., **22** (1993) 731.
2. R. Nigam, S. Srivastava, S. Prakash and M.M. Srivastava, Chem. Spec. and Bioavail. **12**(4) (2000) 125.
3. R. Nigam, S. Srivastava, S. Prakash and M.M. Srivastava, Plant Soil **230** (2001) 125.
4. R. Nigam, S. Srivastava, S. Prakash and M.M. Srivastava, J. Environ. Biol. **23**(2) (2001) 175.
5. Xue Dongsan, R.H. Robert and L.H. Charles, J. Environ. Sci. **7** (1995) 399.
6. J.C. Dupont, G. Casale and R. Krichman, J. Environ. Stud., **12** (1978) 301.

Stable Environmental Isotope Variation in the Karstic Terrain and Delineation of Groundwater Recharge Area in the Western Part of Chhattisgarh Basin, India



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The Amner river basin occupies an area of 1660 square kilometers, a major part of western Chhattisgarh Basin, in Rajnandgaon district, Chhattisgarh (earlier Madhya Pradesh). The study area lies between $21^{\circ}15' - 21^{\circ}45'N$ latitudes and $80^{\circ}20' - 81^{\circ}45'E$ longitudes. The boundaries of the river basin are clearly demarcated by structural hills in the west and distinct water divides on the northern and southern side. Khairagarh and Chhuhikhadan are the main towns in the area (Fig. 1).

The study was initiated using environmental isotopes with the aim to understand the recharge process and movement of groundwater in karstic terrain. Application of environmental isotopes pertaining to hydrogeological investigations has not been carried out earlier in the karstic region of Chhattisgarh Basin.

Amner river forms the principal drainage of the study area, along with its eight tributaries, and flows from west to east and finally joins Shivnath river. The mean annual precipitation is 1050 mm and the annual temperature varies from 9.5°C to 45°C. The study area is of tropical sub-humid type.

Amner river basin forms the western part of the Chhattisgarh Basin. Rocks of Dongarhgarh

Supergroup and Chhattisgarh Supergroup forms the major geological formations [1-4]. The Dongarhgarh Supergroup consisting of Nandgaon and Khairagarh Group, occupy the western portion of the study area. While, the Chhattisgarh Supergroup comprising of Chandarpur and Raipur Group of sedimentary rocks are exposed in the central and eastern portions of the Amner river basin. The geological map is shown in Fig. 2. The Chilpi Group is sandwiched between rocks of Nandgaon and Khairagarh Groups. It forms structural hill range. Two major faults and number of minor faults have been observed on the eastern and western sides of the structural hill range.

The rock sequence of Chhattisgarh Supergroup comprises mainly of alternate sandstone and limestone formations [3,4]. The Raipur limestone occupies a major area as an outcrop in the Amner river basin. Karstification in the Charmuria and Raipur limestone of Raipur Group is observed prominently.

On the basis of systematic monitoring of 169 dugwells for the premonsoon and postmonsoon seasons, covering the entire basin, five major hydroolithounits have been demarcated namely, andesite, Chilpi Group, rhyolite, limestone and sandstone. The Chilpi Group forms an isolated

[illegible]

Fig. 2 Geological map of the Amner river basin.

aquifer system, and has not been considered for the present study.

The water table contour maps indicate that the general groundwater flow direction is towards the Amner river i.e. the axis of the basin, which further moves eastwards to the Shivnath river. The groundwater occurs under phreatic conditions. The limestone forms the major hydrolithounit of the study area, based on geological expanse. Karstification, i.e. development of secondary porosity in limestone [5], has imparted anisotropic behavior of groundwater movement.

Isotope Studies

The well inventory study shows substantial fluctuation in water levels during premonsoon and postmonsoon season. The number of successful bore wells is also not consistent. This may be attributed to the anisotropic karst aquifer. Karst aquifer often comprises an extensive, thick-fissured mass of rock, transmitting the flow of an underground river and its tributaries thus making karst hydrogeology unpredictable. No work has been carried out on application of isotopes related to hydrogeological problems in karst region of Chhattisgarh Basin.

The limestone forms a major hydrolithounit in the study area, and is being tapped to meet the needs of water for drinking and agriculture. The well inventory gives a general idea about the groundwater occurrence and movement. The major ion chemistry and stable environmental isotope analysis helps to identify groundwater recharge area by distinguishable geochemical and isotopic signature [6]. Along with major ion chemistry, isotopic measurements of $\delta^{18}\text{O}$, δD (^2H) and ^3H in water were carried out. A total of fifty-seven samples were collected during January–March 1995 from various sources viz. precipitation, reservoir, river and stream, spring, tubewell and dugwell. The location of samples collected from various sources of the study area is shown in Fig. 1.

Results and Discussion

The groundwater in the study area is fresh in quality, on the basis of electrical conductivity (EC), temperature and Ph and major ion chemistry [7]. A characteristic limestone facies of Ca-Mg-HCO_3 is revealed when plotted on Piper trilinear diagram.

The regression line for samples from the δD - $\delta^{18}\text{O}$ plot is, $\delta\text{D} = 7.14 \delta^{18}\text{O} + 2$, which indicates that the recharge occurs faster after precipitation. The meteoric water confirms that the recharge in the area is due to precipitation and the tubewell samples fall along the regression line demonstrating no significant evaporation [8]. Also, $\delta^{18}\text{O}$ -EC and tritium versus $\delta^{18}\text{O}$ plot confirms that there is no interconnection between the surface waters in the metasedimentary and igneous formations and the karstic aquifer. The tritium content signifies modern origin of groundwater [9].

The data from tubewell samples are preferred over surface water samples as the regional groundwater flow is independent of surface topography and the groundwater flow is due to difference in head. The EC variation in the Amner river basin is uniform, except for an abnormal high concentration at Khairagarh (2300 $\mu\text{S/cm}$), Achanakpur (1264 $\mu\text{S/cm}$) and Ruse (1065 $\mu\text{S/cm}$). This localized high EC concentration can be attributed to direct infiltration of surface runoff from open sewage and/ or agriculture run-off into the karstic aquifer (Fig. 3).

The $\delta^{18}\text{O}$ values progressively get enriched along the axis of the Amner river, from -3.10‰ in the central part, to -2.00‰ at the confluence with Shivnath river. The augen shaped $\delta^{18}\text{O}$ iso-concentration contours around Ruse (-1.80‰), Tekapar Khurd (-2.0‰), Karamtara (-2.08‰) and Kohkabor (-2.17‰), and an uniform enriched contour pattern around Daniya (-2.10‰), Barhapur (-2.40‰), Dandesara (-2.50‰), Achanakpur (-2.60‰) and Hirri (-2.60‰) is indicative of faster recharge of precipitation (Fig. 4). The δD iso-concentration contour plot also illustrates analogous contour pattern that for $\delta^{18}\text{O}$ values (Fig. 5). The gradual

decreasing of the δD values infers a mixing between the groundwater from the base-rock and the groundwater of local recharge. The advantage of plotting δD iso-concentration contours is that it depicts the natural groundwater flow and the concentration is not affected by exploitation. The tritium concentration in the study area is low, but a wide variation from 1.4 TU to 9.8 TU is observed, which is indicative of relatively recent water (Fig. 6).

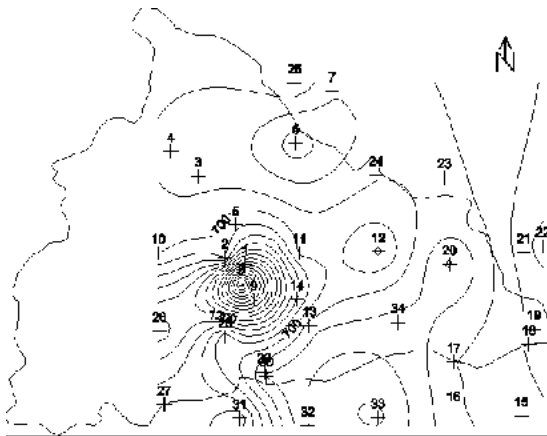


Fig. 3 Variation of EC in the Amner river basin, shown as isolines.

The piston flow model does not apply to karstic aquifer due to groundwater movement along secondary porosity [10].

Conclusions

The present feasibility study has given a perception about the spatial variation of stable environmental isotope content in the water samples from various sources of the study area. This variability can be effectively employed for the assessment of groundwater resources as it provides essential information concerning groundwater occurrence & movement and its origin. The results signify that the infiltration of precipitation is the major component of groundwater recharge. The stable isotope content of water originating at

Fig. 7. Delineation of recharge and discharge areas in the Amner river basin on the basis of variation of $\delta^{18}\text{O}$, δD & T in the Amner river basin. The solid arrow shows the major recharge area and the direction of the groundwater movement. The dashed line shows the discharge area i.e. along the axis of the Amner river.

higher altitude is depleted. There is no hydraulic interconnection between high altitude aquifer and karstic aquifer. This is highlighted after comparison of the stable isotope content of water from elevated region and karstic aquifer. The groundwater holes around Khairagarh and Paiti

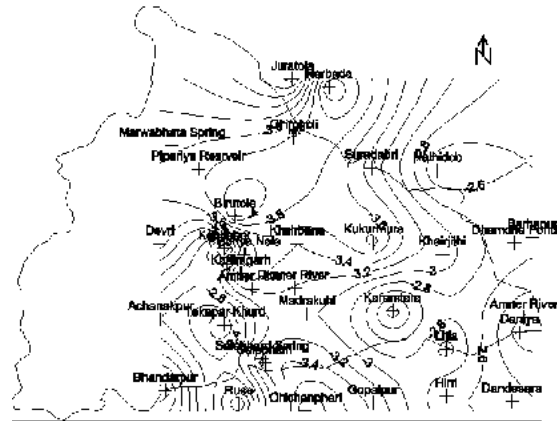


Fig. 4 Variation of $\delta^{18}\text{O}$ in the Amner river basin, shown as isolines.

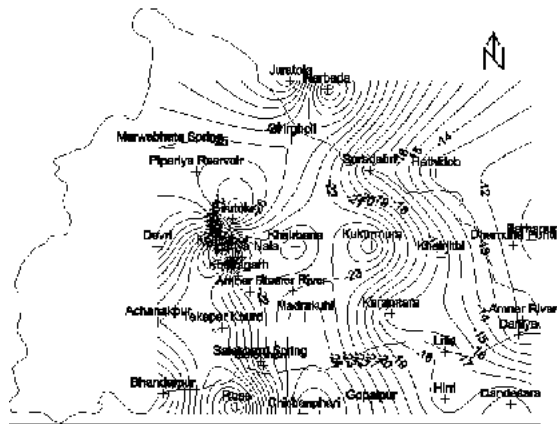


Fig. 5 Variation of δD in the Amner river basin, shown as isolines.

regions suggest the effluent nature of groundwater, which continues from along the axis of the river from Khairagarh to the confluence of Amner river with the Shivrath river. The nature of variability of the stable environmental isotopes around Ghirgholi-Narbada-Suradabri in the north, and Salebharri-Madrakui-Karamtara in the south indicates active groundwater recharge zones in the basin. The inferences as deduced from the present study are shown in Fig. 7. The recharge area is not constrained to the water divide as characterised by the topography on the north and south margin of the Amner river basin, but extends beyond it and interbasinal water transfer cannot be ruled out.

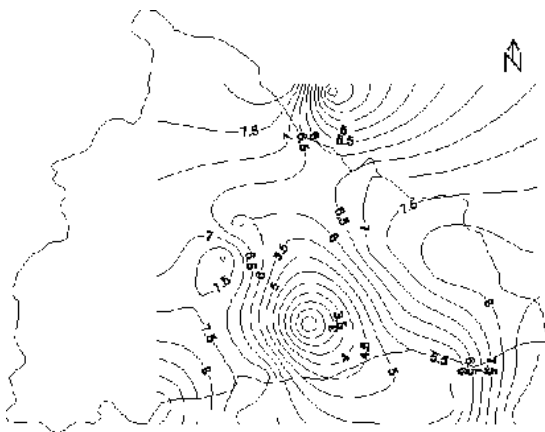


Fig. 6 Variation of Tritium in the Amner river basin, shown as isolines.

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References

1. S.N. Sarkar, J. Sci. Eng. Res. **1** (1957) 237.
2. N.V.B.S. Dutt, Rec. Geol. Surv. India, **93** (1964) 143.
3. K.S. Murti, In B. P. Radhakrishnan (ed.), Purana Basins of Peninsular India.: 239-260. Bangalore: Geological Society of India (1987).
4. D.P. Das, A. Kundu, N. Das. D. R. Dutta, K. Kumaran, S. Ramamurthy, C. Thanavelu and V. Rajaiya, Indian Minerals, **46** (1992) 271.
5. D. Ford and P. Williams, Karst geomorphology and hydrology. London:Unwin Hyman Inc. (1979)

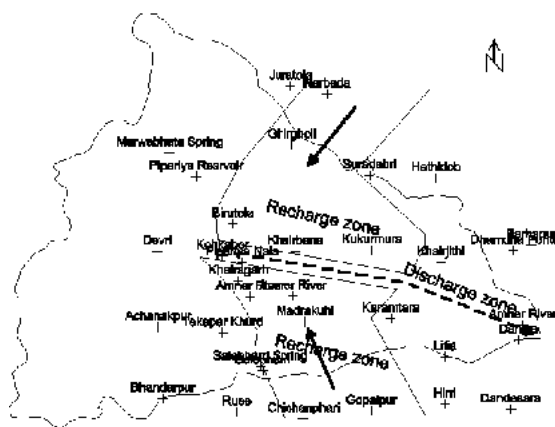


Fig. 7 Delineation of recharge and discharge areas in the Amner river basin on the basis of variation of $\delta^{18}\text{O}$, δD & T in the Amner river basin. The solid arrow shows the major recharge area and the direction of the groundwater movement. The dashed line shows the discharge area i.e. along the axis of the Amner river.

6. B.R. Payne, Practical applications of stable isotopes to hydrological problems. Stable isotope hydrology: Deuterium and Oxygen-18 in the water cycle, Technical Report Series No. 210, International Atomic Energy Agency, Vienna, p. 303-334 (1981).
7. IS:10500 1991. Indian standard drinking water specification (First Revision). Bureau of Indian Standards, New Delhi, 5 p.
8. H. Craig, Science, **133** (1961) 1702.
9. N. Bodhankar, S. Upadhyaya, K. M. Kulkarni, S. V. Navada, U. K. Sinha & U. P. Kulkarni, In Marinos, Koukis, Tsiambaos & Stoumaras (eds) Engineering Geology and the Environment.: 1617-1622. Balkema, Rotterdam (1997).
10. J.Ch. Fontes, In Guidebook on nuclear techniques in hydrology. International Atomic Energy Agency, Vienna.: 285-317 (1983).

Development of Wide-line and Pulsed NMR Spectrometers



Dr. Ramakrishna Damle obtained his M.Sc. in Physics in 1983 from Mysore University, Mysore and Ph.D. from IISc in 1990. He is at present reader in physics in Bangalore University, Bangalore. His areas of interest are NMR/ESR study of molecular dynamics and phase transitions in inorganic solids, Study of radiation induced effects in semiconductor devices and NMR and conductivity studies in polymer based solid electrolytes. He has collaborative programme with Indian Institute of Science, Bangalore, ISRO Satellite Centre, Bangalore, Nuclear Science Centre, New Delhi, Electronics Division, BARC, Mumbai and Variable Energy Microtron Centre, Mangalore University. He is Secretary of Indian Physics Association, Bangalore Chapter.

Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most powerful tools in modern science. The application of NMR spreads from physics to chemistry, bio-sciences, material research and medical diagnosis. NMR is the only method for determining the structure of the molecule in the liquid state. In the solid state also, NMR is used as a valuable supplement to X-ray spectroscopy in the structure analysis.

With the advancement in electronic instrumentation, highly sophisticated modern NMR spectrometers are now available for structure and dynamics elucidation of molecules both in the liquid and solid state. Commercial NMR spectrometers employ a superconducting magnet and are thus very expensive and difficult to maintain. These spectrometers are not made in India. Further, high resolution NMR spectrometers are not routinely employed for time domain experiments (for example, measurement of NMR relaxation times) as these measurements involve enormous machine time. Thus, for those interested in time domain experiments, it is necessary to develop one's own NMR spectrometers. In a few laboratories in India and abroad too, the NMR study of molecular dynamics and phase transitions are being carried out using home made spectrometers. These low cost, less sophisticated NMR spectrometers are suitable for making measurement of line width and relaxation times.

Traditionally, NMR in bulk materials can be observed in two ways: (i) Continuous wave technique and (ii) Pulse technique. In the continuous wave or wide-line NMR, the static magnetic field is linearly swept through the resonance at a fixed radio frequency. The resonance signal is observed as a line of Lorentzian shape for liquids and a Gaussian shape for solids. The intensity of the resonance absorption signal, the width and shape of the signal contain information about the structure and dynamics of the system being investigated. This wide line technique is now being widely used for the study of non-resonant rf response in ceramic superconductors [1]. In the pulse technique, a short and high power rf pulse is applied to the sample at a discrete frequency and the nuclear spin system is observed after the rf is turned off. The free induction decay (FID) signal induced by the nuclear spin system in response to a sequence of rf pulses provides a method for determining the spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2). Since T_1 and T_2 are related to the microscopic details of the system, their measurement as a function of temperature and pressure gives valuable information about the dynamics of the spin system.

A wide-line and a pulsed NMR spectrometer have been developed in the Department of Physics, Bangalore University under a DAE (BRNS) sponsored research project. This is perhaps the first of its kind in an University in the country. These spectrometers have been assembled around an

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existing commercial electromagnet (Bruker B-MIN C5S). This electromagnet has a pole gap of 2.8 inch, 8 inch diameter pole pieces with automatic field sweep facility. These spectrometers are being utilized for the study of molecular dynamics and phase transitions in inorganic solids of technological importance. A low temperature gas flow cryostat has been fabricated to make measurement as a function of temperature in the range of 77-300 K. A brief description of the different sub units of both the NMR spectrometers is given below. Important conceptual aspects are discussed without referring to detailed circuitry.

Wide line NMR Spectrometer

The block diagram of the wide-line NMR spectrometer operating in the frequency range 5-15 MHz is shown in Fig.1. It consists of an electromagnet capable of producing a steady and homogeneous magnetic field, a sensitive low-level radio frequency oscillator, a lock-in amplifier and a signal acquisition system. The tank coil of the oscillator, containing the sample in vacuum sealed glass tube, projects inside the pole pieces of the electromagnet. Due to long relaxation times encountered in solids, oscillators which work at very low levels with good stability, are required to avoid saturation. A home made Robinson's oscillator has been employed in the present set up [2]. A wide line NMR spectrometer operates at a fixed frequency and the spectrum is normally scanned by the linear variation of the static magnetic field. When the separation between the two nuclear spin energy levels is equal to the quantum of energy of the incident photons, absorption takes place and one gets an absorption spectrum. The resonance absorption by the sample is indicated by a change in the detector current. The detection of the NMR signal is accomplished by Phase Sensitive Detection (PSD) used in conjunction with magnetic field modulation. The magnetic field modulation is provided by the two Helmholtz coils placed on either side of the sample coil along the axis of the static magnetic field. The coils are driven by a low frequency generator. If the amplitude of modulation is small compared to the line width, the amplitude of the NMR signal will be approximately proportional to the slope of the absorption curve at the center point of modulating field. The output of the

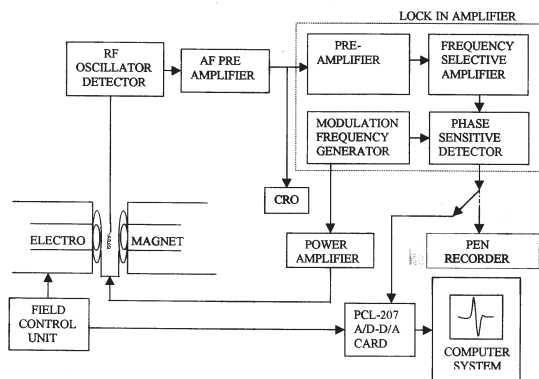


Fig.1 Block diagram of the wide-line NMR spectrometer

oscillator-detector at the modulation frequency undergoes narrow band amplification. Further reduction in noise is achieved by PSD using a lock-in amplifier which is capable of measuring signals buried in noise. The PSD output which is proportional to the input signal is rectified and filtered by a selected RC combination and the signal can be recorded. For the present spectrometer, we have used a locally made lock-in amplifier (AMCO Model EE 201). A low frequency ac signal at 126 Hz, derived from the in built oscillator in the lock-in amplifier, is power amplified using a Phillips power amplifier (LBD 8120) and then fed to the Helmholtz coils for magnetic field modulation. The detected signal from the oscillator-detector is amplified using an audio amplifier (ECC 83 triode amplifier) and then fed to the lock-in amplifier for phase sensitive detection.

Customarily, the NMR signals are recorded using a pen recorder. However, pen recorders are not only cumbersome to use but are rather expensive. With the availability of a variety of digital signal processing interface cards, it is possible to acquire the signal onto a computer through ADC interface. In the present spectrometer, we have used a 12-bit PCL-207 interface card for signal acquisition onto a computer. PCL-207 is a low cost AD/DA multifunction data acquisition card for IBM PC/XT/AT and compatible computers [3]. The A/D interface card is inserted in the CPU of the computer and is connected to outside environment through a terminator board. There are two ways to accomplish

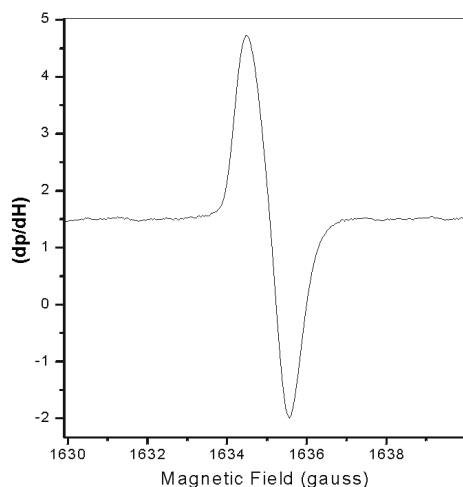


Fig. 2 ^1H NMR signal in glycerin at 7 MHz

the PCL-207 functions in application programs. The first method is to use PCL-207 driver routines and let the driver handle the I/O port interface. The second method is to use I/O port instructions in the application program directly. The former method gives greater flexibility in dealing with special application requirements. In the present work, a simple program in GW BASIC is used to acquire the NMR absorption signal as a function of the magnetic field swept through the resonance. As the magnetic field is swept through resonance, the digitized data of the first derivative signal of nuclear absorption is stored and the plotting of the data points gives the signal as a function of the actual magnetic field swept through the resonance. Fig.2 shows the ^1H NMR signal in standard sample of glycerin at an operating frequency of 7 MHz. Appropriate scaling incorporated in the program facilitates the calibration of the magnetic field on the X-axis, so that direct measurement of the line width is possible on screen without obtaining the hard copy of the signal. This method thus eliminates the calibration run which is usually required when the signal is recorded using pen recorders. Thus the automation of signal acquisition is found to be not only efficient and handy for data analysis but also inexpensive as compared to pen recorders [4].

The most convenient and widely used method of detecting the NMR absorption in a system is to use magnetic field modulation and sweep the strength of the dc magnetic field through resonance. Apart from

this we have tried other uncommon and complex modulation and detection schemes such as (i) frequency modulation and field sweep (ii) field modulation with frequency sweep and (iii) frequency modulation and frequency sweep. These schemes although known for a long time, are never routinely used in the literature for NMR work due to experimental difficulties. Our observation is that all these schemes more or less lead to the same shape and intensity of the signal. However, scheme (iii) leads to drastic instabilities in the oscillator frequency leading to distortion in the signal and thus this scheme is rather impractical [5].

Pulsed NMR Spectrometer

The pulsed NMR spectrometer has a number of requirements, some of which could be mutually exclusive. The block diagram of the home assembled pulsed NMR spectrometer operating in the frequency range of 1-30 MHz is shown in Fig. 3. The minimum requirements of a pulsed NMR spectrometer are as follows:

1. A pulse programmer to provide necessary pulse sequences.
2. A transmitter (power amplifier) capable of delivering short (1-20 μsec) powerful (100-1000 V) rf pulses. The rf pulse should have short rise and fall times (< 0.5 μsec , typically).
3. A network (probe) to match the transmitter to the sample coil and the sample coil to the receiver.
4. A receiver (~ 80 dB gain) capable of recovering quickly (~ 10 μsec or less) from overloads.
5. A signal averaging instrument to improve the signal to noise ratio and to measure the FID amplitude.

Many pulsed NMR spectrometers have been described in the literature [6-8].

Pulse Programmer

Early pulsed NMR spectrometers employed microprocessor based pulse programmers. Programmable pulse generator built around Intel microprocessors peripheral 8253 without a controlling microprocessor has also been used by

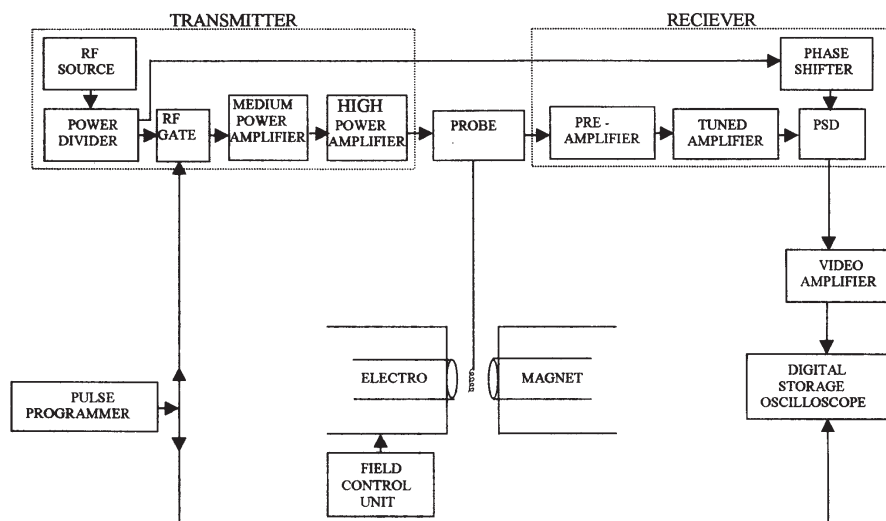


Fig. 3 Block diagram of the Pulsed NMR spectrometer

some. With the availability of fast computers and add on cards, the complexity of the pulse programmer has now been reduced to a single board. In the present Pulsed NMR spectrometer, a programmable pulse generator built using a PCI DIOT card is used [9]. PCI-DIOT card is a PCI based digital input/output timer card for IBM compatible PC's. This card contains two 8255 programmed peripheral interface (PPI) which provide 48 programmable I/O lines and one 8254 programmable interval timer with 3 programmable counters/timers. The card can be plugged into any one of the free PCI slots of the system. The system clock of the computer is utilized to drive the timer and the timer is programmed using 'C' language to generate the required pulse sequences (2 pulse, 3 pulse and saturation burst sequence). The pulse width, delay between pulses and repetition time of the sequence can be independently programmed over a wide range. The pulse widths are variable from 1 μ s to 127 μ s; the delay between the pulses is variable from 10 μ s to several seconds; the repetition time is variable from 1 to 100 s. A short nanosecond pulse generated at the end of each sequence is used for triggering the Digital Storage Oscilloscope (DSO) for data acquisition. This method of generating pulse sequences is found to be efficient and easy to use as compared to microprocessor based

pulse programmer and is easily programmable even for complex pulse sequences.

The rf Unit

The rf unit consists of a signal source (Systronics standard signal generator model 1103) capable of working between 1 to 72 MHz. The rf signal is amplified by a wide band amplifier (United Systems AH-520, 1-100 MHz) and is given to a power divider which gives two in-phase isolated (50 dB) outputs. One of these outputs is used as the rf input to the transmitter and the other is used as the reference for the phase sensitive detector.

The Gated Transmitter

The output from the rf unit is gated and power amplified before coupling to the sample. The gated transmitter has three stages (i) the rf gate (ii) the medium power amplifier and (iii) a high power amplifier. A Double Balanced Mixer (DBM) and a medium power amplifier manufactured by United Systems Engineers Pvt. Ltd. are used for gating and initially amplifying the gated rf to a voltage of about 20-30 V peak-to-peak into 75 ohms. These units are custom built to the specifications. The output of the medium power amplifier is further amplified by a rf amplifier using a National Electronics 3E 29 dual tetrode working in the push-pull configuration. Since the push-pull amplifier has an input

impedance of 600 ohms, the grids are gated through the wide band transformer North Hills NH 0900 BB (100 KHz – 30 MHz) by the synchronous pulses which are amplified by a pulse amplifier. The output of the push-pull amplifier is taken through another wide band transformer (North Hills NH 1703 BA) having the output impedance of 75 ohms. The transmitter rf pulse is variable from 100-300 V p-p.

The Pulse NMR Probe

The most important part of the pulsed NMR spectrometer is the matching network (probe) which couples the power from the transmitter to the sample coil during pulse ON period and converts the precessing magnetization into a detectable signal at the input of the receiver immediately following the pulse. The probe should also decouple the receiver from the transmitter during the pulse ON period. We have used a single coil probe proposed by Clark and McNeil, where a single coil is used as a transmitter and receiver [10]. This single coil series tuned LCR network is simpler and has several advantages over other networks described in the literature, in terms of maximum power efficiency. Crossed diodes and $\lambda/4$ transmission lines are used to protect the receiver from transmitter pulse overload.

Receiver

The receiver consists of a fast recovery preamplifier, a wide band amplifier, a phase sensitive detector. A receiver amplifier with a total gain of about 80 dB and recovery time of about 2 μ s, custom built to specification by United System Engineers Pvt. Ltd. has been used for the purpose. The signal output of the phase sensitive detector (a DBM is used for the purpose) after filtering and amplification is acquired by a 100 MHz DSO for signal averaging and measurement.

The assembling of the pulsed NMR spectrometer has been completed and is being optimized for reproducibility of the signal in test sample. Eventually, the spectrometer will be used for the measurement of proton NMR relaxation times as a function of temperature in ammonium and hydrazinium based diamagnetic solids. It is felt that

there is enough scope for improvisation in the performance of both the wide line and pulsed spectrometers which will be incorporated in a phased manner in due course of time. Figs. 4 and 5 exhibit the photograph of wide-line and pulsed NMR spectrometers respectively.

Acknowledgements

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References

1. S.V. Bhat, Amit Rastogi and Y.S. Sudershan, Solid State Comm., **89** (1994) 633.
2. F.N.H. Robinson, J. Sci. Instrum., **36** (1959) 481.
3. PCL -207 User's Manual, Dynalog (India) Limited, 1996.
4. K.J. Mallikarjunaiah, S.R. Kulkarni and R. Damle, Being Communicated to Indian Journal of Pure and Applied Physics.
5. N. Sasidhar, K.J. Mallikarjunaiah and R. Damle, J. Instrum. Soc. India, **32(1)** (2002) 1.
6. W.G. Clark, Rev. Sci. Instrum., **35** (1964) 316.
7. R.K. Shenoy, J. Ramakrishna and K.R. Jeffrey, Pramana, **14** (1980) 363.
8. R.E. Ader, A.R. Lepley and D.C. Sanngio, J. Mag. Reson., **29** (1978) 105.
9. K.J. Mallikarjunaiah, J.T. Devaraju and R. Damle, Proc. Of National Symposium on Instrumentation (NSI-27), 27-29, Nov 2002, Coimbatore, India.
10. W.G. Clark and J.A. McNeil, Rev. Sci. Instrum., **44** (1973) 844.

Designing a Simple BOD Biosensor



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Determination of pollution in various water bodies is an important concern in environment management. The most common pollutants in large water bodies are organic products mainly coming from sewage and industrial effluents containing both organic and inorganic components. Other kinds of pollution, e.g., thermal pollutions are only recently being recognized. Some of the pollutants have a large residence time (e.g., heavy metals; DDT) whereas some are relatively rapidly degraded by the microbial activity of the natural water body. Decomposition of natural organic compounds by microbes can take place by either (i) aerobic (processes that use oxygen for oxidation) or (ii) anaerobic (processes that do not use oxygen and therefore produce only a partially oxidized product) mechanisms. Aerobic oxidation consumes dissolved oxygen and produces a more completely oxidized product. However, we must ensure that sufficient dissolved oxygen is present in the water body for complete oxidation. If the dissolved oxygen concentration is significantly reduced, it is likely to affect other aquatic life (e.g., fish) severely.

It is therefore important to have an estimate of the amount of oxygen required to completely oxidize the pollutants present in a water body by microbial action. This quantity, called Biological Oxygen Demand (BOD) is an important parameter in any studies on pollution. Although this measure has its own limitation, e.g., many of the industrial pollutants are not easily degraded by common microbes present in water body, this is an important quantity that is required to be assessed in any study on pollution. Conventional techniques are simple in principle but are laborious and time-consuming. We hereby report on our attempt on a microbial based BOD biosensor using yeast as a model.

The basic principle of the measurement is essentially simple. We measure the concentration of the dissolved oxygen using an oxygen electrode. In presence of the pollutant, the yeast present on the surface of the electrode consumes dissolved oxygen and this decrease is monitored. The resultant decrease is proportional to the pollutant concentration (BOD) within the limits of the experimental setup.

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For reasons of operational simplicity, the yeast (common Baker's yeast; *Saccharomyces cerevisiae*) was immobilized in a cross-linked polyacrylamide gel. This gel is supported by a semi-permeable membrane close to the oxygen electrode. During the experiment, dissolved oxygen has to diffuse through this gel to reach the electrode. During this period, oxygen is actively consumed by the microbe in presence of the pollutant. This results in a net decrease in the response current.

Materials and Methods:

Glucose oxidase (EC: 1.1.3.4; Sigma Catalog No: G-2133), Catalase (EC: 1.11.1.6; Sigma Catalog No: C-40) Acrylamide (Sigma Catalog No: A-8887), N, N'-methylene-bis-acrylamide (Sigma Catalog No: M-7256), were obtained from Sigma Chemical Co, Mo. Baker's yeast (*Saccharomyces cerevisiae*), Potassium persulfate, TEMED (N, N, N', N' Tetraethylenediamine), were obtained locally. All buffers and salts were from Qualigens, India. All reagents are of GR grade.

The experiments consists of two parts a) setting up the oxygen electrode and its properties (optimization of operating parameters) and b) preparation of the immobilized polyacrylamide gel containing trapped active yeast cells. For pollutants, a standard solution of glucose and glutamate has been used. The rate of oxygen depletion was studied and modeled using a suitable kinetic theory.

The Oxygen electrode: Covering a simple gold electrode sealed in plastic rod with double dialysis membranes, this electrode, when used at a potential of -0.7 V (vs a Ag/AgCl reference) makes oxygen electrode. The dialysis membrane is used to (1) to prevent fouling of the electrode by adsorption of macromolecules and (2) to hold the polyacrylamide gel in close proximity to the electrode. However, the dialysis membrane does introduce a diffusion barrier and naturally delays the response of the electrode. This is unavoidable, as no (bare) oxygen electrode can be reliably operated in a solution containing biological macromolecules without some kind of protection.

Preparation of the polyacrylamide gel: Commercial baker's yeast (100 mg) in dry form is activated at room temperature in 500 mL of water

consisting of 500 mg glucose, 100 mg NaHCO_3 and 100 mg NaCl. This solution is left for 12 to 14 hrs for activation. The yeast is then harvested by centrifugation at 5000 rpm for 10 min. The pellet was washed twice in phosphate buffer (20 mM pH 7.0), mixed with 20% acrylamide solution (2.5% cross-linker), 10 μL TEMED, and potassium persulfate and allowed to polymerize between two glass plates (using 1 mm spacer). After polymerization, the gel is cut into regular circular disks (using a disposable pipette tip) and the cut disks are stored in 2% KCl solution at 4°C . The gel finally contains 1 mg of yeast cells per ml of the gel. This type of entrapment of yeast cells has an advantage that they are cheap, portable and have long shelf life of about fifteen days to one month. This process is simple, gentle and can be used for a large number of different microbes with minor modifications.

Instrumentation

Clark type of oxygen electrode is used in our experiments. The apparatus consists of standard three electrodes setup consisting of a gold electrode covered with double dialysis membrane, which is held in place using tygon 'O' ring as shown in the Fig. 1. The electrode is a 2 mm diameter gold rod fixed in a plastic holder such that only one end is exposed. Immobilized yeast cells disk is sandwiched in between the dialysis membranes and placed over the surface of the electrode. This completes the fabrication of working electrode to measure dissolved oxygen depletion rate. The other two-electrodes consist of the reference electrode (silver-silver chloride, in 1M KCl) electrode and a platinum counter electrode. KCl (100 mM) was used

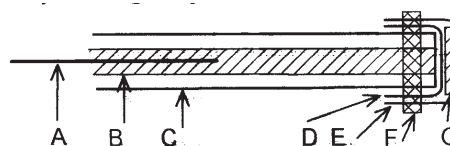


Fig. 1 Schematic diagram of the electrode. Legends: A: electrical connection; B: gold rod; C: plastic (bakelite) casing; D and E: dialysis membranes; F: rubber band; G: gel containing trapped enzyme. The diagram is not to scale and has been expanded to reveal details.

as supporting electrolyte. When a proper voltage (-0.7 V vs the reference) is applied, a current is produced which is proportional to oxygen concentration, which is monitored as a function of time. Details of electrochemical principles are given elsewhere [1,3].

For electrochemical work, a CH Instruments potentiostat (model 660A) has been used. The instrument was connected to the cell in the standard way. The software was installed on a PC (IBM compatible machine running the Windows 2000 OS) and was configured as described for individual experiments. The resulting curves were stored in a file and analysed using independent software (Sigmaplot v6.0; Jandel Scientific).

Results and Discussions

Standardization of the Electrode

It is essential before proceeding further to ensure that the oxygen electrode setup is working satisfactorily. For this purpose, we have used an enzymatic method rather than a chemical method. This is carried out as follows:

1. We setup the potentiostat for amperometric studies- to measure, we get a current vs. time. The current initially is high but it stabilizes in a few seconds to a constant value that represents the concentration of the dissolved oxygen in the buffer. We have used 5 mL of 100 mM KCl containing 20 mM phosphate buffer (pH 7).
2. After a short while (when the current has stabilized), we added a small amount of glucose solution (representing the pollutant). In our experiments, we have used 5 mM final concentration of glucose.
3. Glucose being electro-inactive, has no effect on the current. Glucose is not spontaneously oxidized by dissolved oxygen.
4. After a short period, we added a small amount of the enzyme mixture. In our experiment, we have added ~1 unit of Glucose oxidase and ~100 units of catalase for the 5 mL reaction mixture.
5. We observed an immediate decrease in the current. This corresponds to the decrease in the concentration of dissolved oxygen.

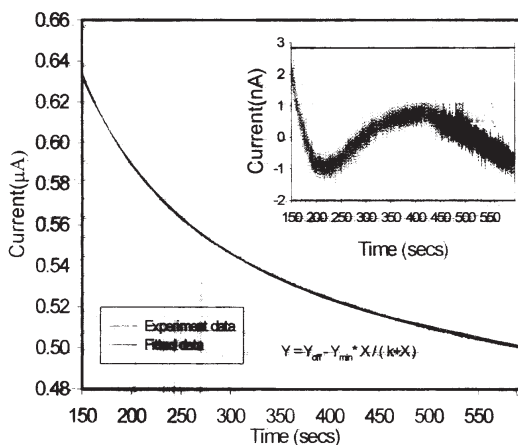
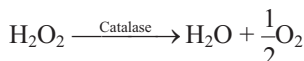
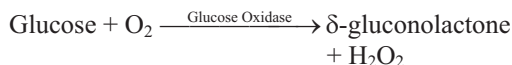


Fig. 2 The current vs time graph for the oxygen electrode setup. The experimental and fitted data fit very well. The inset shows a plot of the residuals (note scales) for the same graph. The fit equation is based on a rectangular hyperbola with an offset (to account for the background current). Details of the experimental conditions are given in the text.

6. The current- time data were saved in the PC and analysed by software.
7. The overall reactions are shown below:



It may be mentioned here that for final studies, we have used a solution of glucose and glutamate as pollutant (as standard). Total run time for this experiment was about 600 s, but this naturally depends on the activity of the enzymes.

A typical plot of current as a function of time obtained in our experiment is seen in Fig. 2. We also may mention here that in an open vessel, it is practically impossible to have the supporting solution completely free from dissolved oxygen. Therefore the current does not decay to zero in any given experiment. In addition, there may be other (traces of) redox impurities that may contribute to the background current.

TABLE 1. Rates of oxygen consumption by immobilized yeast cells.(rates are expressed as decrease in current (μA) in 200 secs, determined graphically)

No	Substrate added (μL in 5 mL)	Decrease in current
1.	50	i) 0.019 ii) 0.024 iii) 0.006
2.	100	i) 0.021 ii) 0.033 iii) —
3.	150	i) 0.025 ii) 0.036 iii) 0.019
4.	200	i) 0.052 ii) 0.105 Iii) 0.026

Results

Figure 2 shows the results of the oxygen electrode setup using enzymatic oxygen depletion. The supporting electrolyte (5 mL) was 100 mM KCl with 20 mM phosphate buffer (pH 7). After ~ 100 s, ~ 100 units of catalase and 1.6 units of glucose oxidase were added. At ~ 150 s, 10 mmoles of glucose were added. The data collected during the interval 150 to 600 sec were analyzed and fitted using a hyperbolic curve.

The reason for this choice of graph is based on the Michaelis Menten equation used in homogeneous enzyme kinetics. Instead of measuring the formation of the product, we observed the depletion of the reactant (O_2). An offset term has been added to account for the background current.

The experimental fit is excellent (the two curves overlap so well that they cannot be distinguished) and the residuals are shown in the inset graph. It is to be noted that while the currents are in the range of microamperes, the residuals are of the order of nanoamperes.

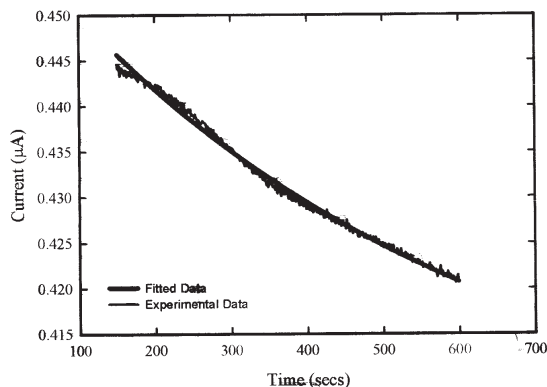


Fig. 3 A typical graph obtained using the immobilized yeast gel. The fitted data is seen as a thick solid line whereas the experimental data is the thinner noisy graph. For reasons of clarity, only 10% of the sampled data points are shown. The fit is not very good in the early parts of the graph (as expected) but the graph stabilizes after a couple of minutes.

Studies on BOD

Although the experiment described above fitted well with theory, it cannot be applied in the case of immobilized yeast biosensor. The gel entrapped yeast (Fig. 1) consumes dissolved oxygen in a heterogeneous reaction and the rate is expected to be diffusion controlled. The amount of yeast present is relatively small and therefore the rate of consumption of dissolved oxygen is also small. Thus a double exponential graph is expected (to take care of the diffusion and biochemical reaction) with a constant term (offset). We fitted the oxygen depletion curves using a five parameter equation: $y = y_0 + a e^{-bt} + c e^{-dt}$ with good success. The experimental fit is not expected to be as good as in the earlier case, as our system is structurally more complex. The results are presented in Table 1. A typical oxygen depletion graph is seen in Fig. 3. The approximately linear region (slope) of the current vs time graph from 300-500 seconds (Fig. 3) were used for comparison.

From the experimental graph, the slopes were determined manually in the range of 300-500

seconds and the results were used as such in Table I for different concentrations of yeast and pollutant (10 μ L of 10 mM glucose and 10 mM sodium glutamate).

The substrate used was a stock solution of 1 mM glucose and 1 mM sodium glutamate in water. The decrease was measured from 300s to 500s graphically. Initial rates were much higher but had a larger variation. The three values reported in column 3 were obtained in three different experiments using fresh gels.

From this table we note that there is a clear trend (increase in the rate of oxygen consumption with increase in pollutant concentration) but there is significant variation from one experiment to another.

Conclusions

BOD Biosensors play an important role in environmental monitoring of pollution of water bodies[2, 4]. Use of these biosensors help to analyze pollution in a given sample. The setup we have developed can be optimized, the gels can be mass produced, bonded to cellophane or nylon membranes and can be stored (after drying). The membranes are not reusable and have to be replaced after each use. The final system must include an auto-calibration feature to minimize variation from

membrane to membrane. We also need to develop compact electronics so that the whole setup can be used as a portable device.

Acknowledgements

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References

1. A.J. Bard and L. R. Faulkner, Introduction and overview of electrode Processes in Electrochemical Methods, Fundamentals and Applications, John Wiley and Sons, New York, 1980, pp 1-43.
2. S. F. D'Souza, abstract presented at the New Advanced Materials in Molecular Electronics (NAMME) 10-11 December 2001 (NPL), New Delhi.
3. P T Kissinger and W R Heinemann, Small amplitude controlled potential Techniques in Laboratory Techniques in Electroanalytical Chemistry (2nd edition), Marcell Dekker Inc., New York, 1996, pp 141-164.
4. S F D'Souza, Microbial Biosensors, Biosensors and Bioelectronics, **16(6)** (2001) 337.

Microwave Assisted Synthesis and Characterization of Organo-luminophors for Light Emitting Devices



Dr. S. R. Patil, Reader, Department of Chemistry, Shivaji University, Kolhapur, started his research carrier in the field of luminescence spectroscopy of organic semiconducting molecular materials. Dr. Patil is the principle investigator of BRNS research project sanction no. 98/37/8. He obtained his Ph.D. degree in 1992 from Shivaji University. He has set up a fluorescence spectroscopy laboratory in the University department through the financial support received from Department of Atomic Energy, Government of India. He has actively participated in the Research Programme, Work- shops organized by DAE/BRNS, IUC, Indore to plan the experiments on photophysics beam line at INDUS-I. He has published more than fifteen papers in scientific journals of national and international repute.

Dr. P. N. Bhosale, Reader, Department of Chemistry, Shivaji University, Kolhapur, is Co-investigator in BRNS research project. He has developed chemical deposition technique in the laboratory to prepare thin films of mixed sulphide-selenide metal films and their structural and photovoltaic performance studies. His contribution in this area is significant and about fifteen papers are at his credit.



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Introduction

Doped organo-luminophors are extensively used as emitting materials in fabrication of electroluminescent diodes and also in plastic scintillators [1,2]. Hundreds of luminophors are being synthesized and investigated every year with a

view to meet new demands for phosphors in electronic industries. The synthesis involved intentional doping of basic materials emitting towards blue by fluorescent impurities emitting towards red of the visible region of the electromagnetic spectrum. The excitation energy

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transfer from basic host material to impurities (guests) and the energetic interactions between them have given the emission towards the red [3]. The emission behaviour has been characterized by excitation and fluorescence spectroscopy. The doped systems were prepared by solid state reaction techniques involving conventional heating in electrical furnace. We have contributed significantly in the field of phosphor preparation and their characterization [4-7]. However, conventional synthesis required controlled heating and long processing time, which often results with larger particle size and inhomogeneous crystals. The doped crystals of host containing impurities over a limited range were prepared because of saturation effect at higher concentrations, which affects the emission properties. Many times' excessive heating has resulted into charring or decomposition of the components.

A microwave assisted synthesis method developed in our laboratory for doping of organic semiconductors, has given organic mixed crystals having narrow particle size distribution, crystallinity and easy sinterability [8]. Heat produced due to microwave induced rotation of dipoles within the materials dissipates uniformly and heats the materials without charring. More than hundred organo-luminophors have been prepared by microwave heating using domestic microwave oven without temperature measurement. The doped crystals were prepared within a few minutes heating and by slow cooling. In the present article we have given as an example microwave assisted synthesis and fluorescence characterization of doped naphthalene luminophors.

Experimental

The calculated amounts of host and guest materials were intimately mixed and placed in silica crucible. The crucible with lid was heated in microwave oven (BPL Model 600-T) using 2450 MHz microwave radiations. Microwave dielectric heating uses the ability of materials to transform electromagnetic energy into heat which propagate through the material and heats it, removing the need to heat the container. The molten mass of the components were cooled slowly under the same environment to grow mixed crystals of the doped host material. The content was crushed to fine

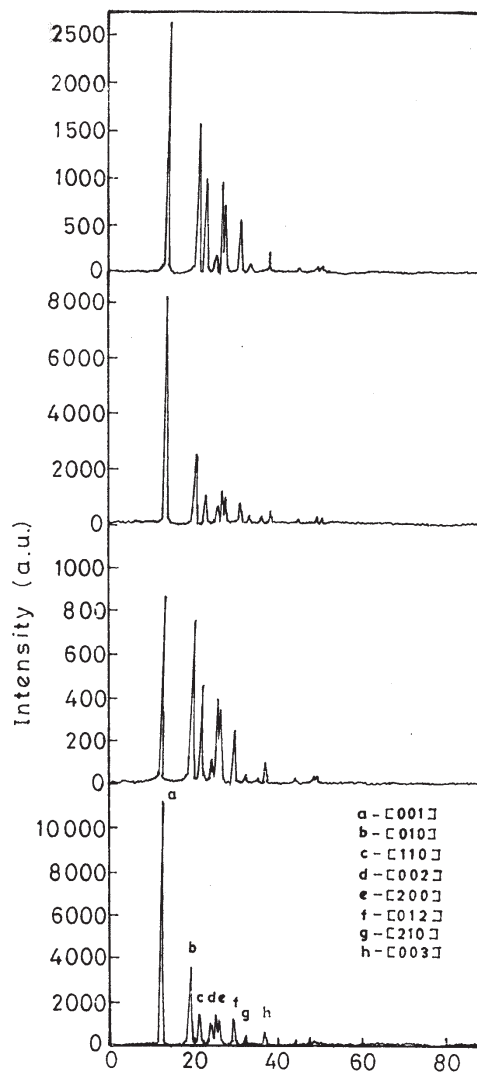


Fig. 1 XRD profile of anthracene and tetracene doped naphthalene

powder and was undertaken for structural and fluorescence characterization.

Results and Discussion

X-ray Diffraction Studies of Mixed Crystals

Figure 1 shows XRD patterns of mixed crystals of doubly doped naphthalene luminophors. The spectra were recorded as a function of tetracene concentration. Figure 1 reveals sharp and well defined peaks indicating crystalline behaviour of the

luminophors. The XRD pattern of pure naphthalene is used as a fingerprint with which the spectra of doped naphthalene are compared. It is observed that the position of the peaks (2θ values) does not change even after doping. No additional peaks are seen in the XRD profile of doped samples, which is an indication of formation of homogeneous mixed crystals. The system has great advantage that it forms excellent solid solutions over a wide range of tetracene concentration inspite of differences of their crystal structure. The intense peak appeared at 11.9° (2θ value) used to calculate particle size. For the calculations the peak width at half maximum were used after magnifying the intense peak. The particle size as a function of concentration of dopant is listed in Table 1. It is noted that the particle size decreases as concentration of tetracene increases. The particle size of the order of 155-210 Å indicate that the microwave assisted mixed crystalline luminophors are more fine grained than those reported by conventional heating[8].

Emission Characterization by Fluorescence Spectroscopy

Naphthalene is a wide band gap organic semiconducting material and known to fluoresce in the UV region when excited by 316 nm radiation. Naphthalene crystallizes in monoclinic unit cell and solublize in it most of the polynuclear aromatic hydrocarbons (PAHs) [9]. Sensitization of the anthracene like emission in naphthalene matrix by excitation energy transfer is our earlier report [5]. Tetracene has strong absorption in the emission region of anthracene doped naphthalene. Therefore, mixed crystals of naphthalene doped by anthracene and tetracene were prepared by microwave heating. Fig. 2 presents the fluorescence spectra of pure crystalline naphthalene, anthracene doped naphthalene and anthracene and tetracene doped naphthalene.

The fluorescence spectrum of naphthalene monitored at 316 nm shows a sharp peak at 341 nm. Lack of vibration fine structure indicates the stronger binding between naphthalene molecules in its lattice. In contrast, the fluorescence spectrum of anthracene doped naphthalene (10^{-1} mole) appeared in the region of 380-475 nm is structured and reveals

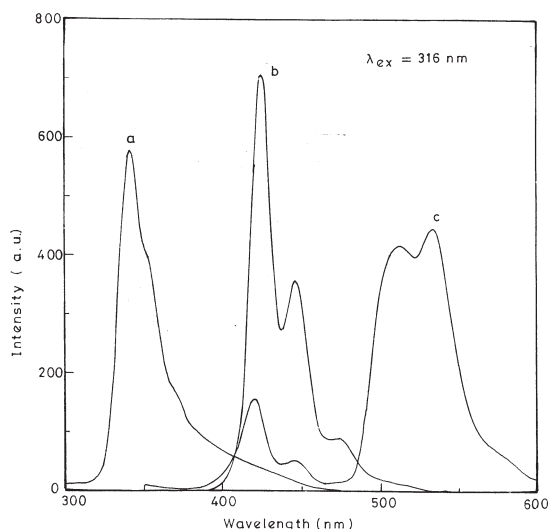


Fig. 2 Fluorescence spectra of pure naphthalene (a), anthracene doped naphthalene (b) and anthracene and tetracene doped naphthalene (c).

vibrational fine structure. The spectrum matches well with the emission spectrum of anthracene solution and does not correspond with that of the crystalline anthracene. The emission is referred to as anthracene like emission having peaks at 420 and 444 nm. The peak at 420 nm is intense. The absence of naphthalene emission in the spectrum suggests the excitation energy transfer (EET) from excited naphthalene (naphthalene exciton) to anthracene impurity. The fluorescence spectrum of anthracene and tetracene doped naphthalene shows additional emission bands in the region of 480-575 nm and emission bands of anthracene like emission is quenched. The two emission bands with wavelength maxima at 492 nm and 526 nm appeared in this region, and are ascribed to the green emission from tetracene molecule. Tetracene does not show fluorescence in crystalline state. But in the present naphthalene luminophor system the green monomeric emission of tetracene has achieved. The observed tetracene emission bands matches with vapour deposited tetracene film emission reported in literature [10]. The quenching of anthracene like emission suggests trapping of emitted radiation by tetracene impurity.

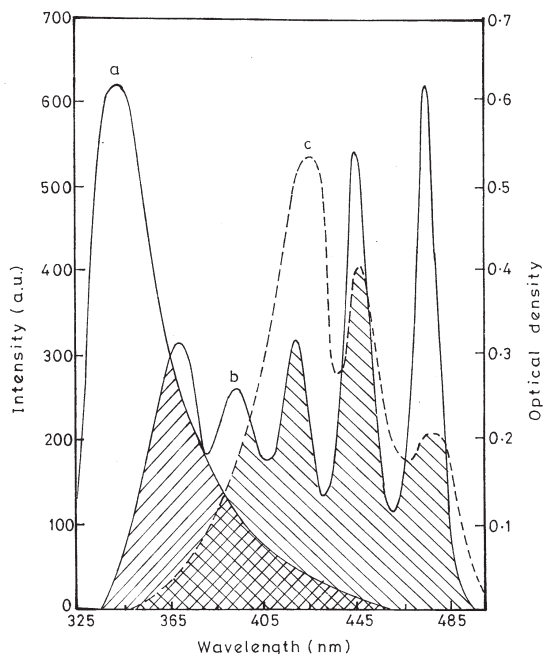


Fig. 3 Region of overlap between absorption spectra of tetracene (b) and emission spectrum of anthracene doped naphthalene (c) and undoped naphthalene (a).

The proposed two step EET route is further supported by the region of overlap indicated in Fig. 3. Figure shows region of overlap between anthracene like emission and absorption spectrum of tetracene. The figure reveals the strong overlap between anthracene like emission and tetracene absorption spectrum. This clearly indicates the probability of significant EET from anthracene to tetracene.

Concentration Dependence of Fluorescence

The naphthalene luminophors containing 1×10^{-3} mole anthracene per mole naphthalene and varying amounts of tetracene have exhibited intense green emission and spectral characteristics found to vary with the concentration of tetracene. Figure 4 shows spectral energy distribution of anthracene doped naphthalene as a function of tetracene concentration. It is seen that as concentration of tetracene increases the emission band peaking at 492

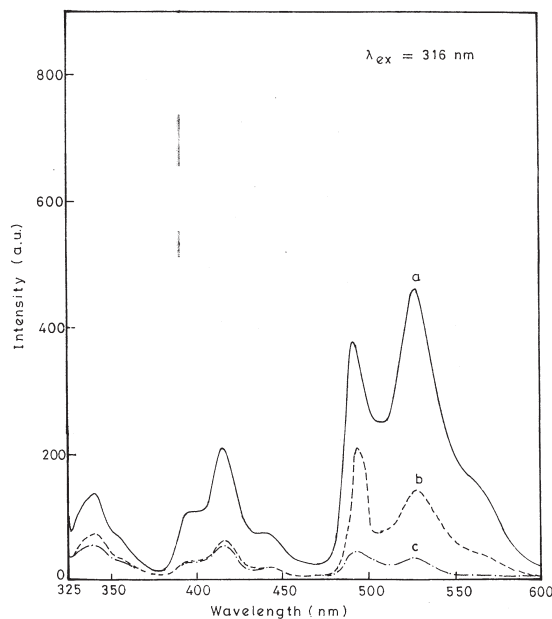


Fig. 4 Spectral energy distribution of anthracene (1×10^{-3}) doped naphthalene containing varying amounts of tetracene.

nm is quenched and second band appeared at 526 nm get enhanced. The fluorescence spectrum of luminophor containing 1×10^{-2} mole tetracene seems to be changed spectrally.

The increase in tetracene emission with dopant concentration has been observed when concentration of both anthracene and tetracene were systematically varied. The details on emission behaviour are given in Table 1. The observed enhancement effect is further supported by the estimation of area under the emission peaks of anthracene like emission and tetracene emission. The ratio of area under the peaks gives relative quantum efficiency and is presented in Table 1. It is noted that as concentration of guest increases the ratio increases. This suggests that the enhancement effect observed in tetracene emission is dependent on its concentration. In addition, the particle size is seen to be decreased with tetracene concentration. The finer particle size increases the surface area,

TABLE 1. Particle size and the ratio of area under the fluorescence peaks of anthracene to tetracene as a function of tetracene concentration per mole naphthalene.

Sr. No.	Concentration of Anthracene mole per mole Naphthalene	Concentration of Tetracene mole per mole Naphthalene	$A_{\text{Anth}}/A_{\text{TCN}}$	Particle size (Å)
1	10^{-3}	10^{-4}	0.76	209.77
		10^{-3}	1.21	203.05
		10^{-2}	1.44	198.0
2	10^{-2}	10^{-4}	0.70	192.5
		10^{-3}	1.14	188.4
		10^{-2}	1.45	176.6
3	10^{-1}	10^{-4}	2.86	171.2
		10^{-3}	3.71	163.0
		10^{-2}	8.38	155.83

which results into efficient EET between neighbouring molecules and rate of emission.

Conclusion

The microwave-assisted synthesis of doped naphthalene luminophors is simple, quick and less expensive method. The particle size determination by XRD studies indicated that the mixed powder luminophors are more fine grained by which the luminophors fluoresce intense green. The microwave heating technique for organic mixed crystal preparation proves to be an exciting tool to obtain new fluorescent materials with better spectral behaviour.

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Reference

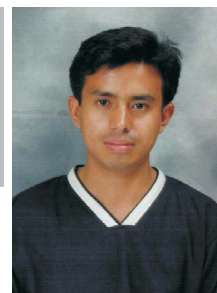
1. P. Posch, M. Thelakkat and H. W. Schmidt, *Synth. Met.*, **102** (1999) 1110.
2. M. Uekawa et al., *Thin Solid Films*, **352** (1999) 185.
3. G.B. Talpatra and T.N. Misra, *J. Phys. Chem., A*, **101**(4) (1997) 407.
4. S.A. Jadhav and S.R. Patil, *Mater. Chem. Phys.*, **60** (1999) 204
5. S.R. Patil and S.B. Patwari, *J. Lumin.*, **82** (1999) 115
6. S.R. Pujari, P.N. Bhosale, P.M.R. Rao and S.R. Patil, *Mater. Res. Bull.*, **37** (2002) 439
7. S.R. Pujari, S.A. Jadhav, P.N. Bhosale, P.M.R. Rao and S.R. Patil, *Indian J. Pure & Appl. Phys.*, **40** (2002) 115
8. S.S. Manoharan, S. Goyal, M.L. Rao, M.S. Nair and A. Pradhan, *Mater. Res. Bull.*, **36** (2001) 1039.
9. G.B. Talpatra and T.N. Misra, *Phys. Stat. Sol. B*, **114** (1982) 73
10. J.A. Katul and A.B. Zahlan, *J. Chem. Phys.*, **47**(3) (1967) 1012

National Centre for Free Radical Research : A BRNS-DAE Project



Prof. B.S.M. Rao, currently Head, Department of Chemistry, University of Pune has been involved in teaching and research in nuclear and radiation chemistry for more than three decades. He had his pos-doctoral training at the University of Manchester on pulse radiolysis and on hot atom chemistry at NIKHEF, Amsterdam. He was awarded the Alexander von Humboldt Fellowship to work at the Nuclear Research Centre, Karlsruhe. He established active collaborative research programs with BARC within the country and outside (MPI f. Strahlenchemie, Muelheim, Germany and MRC Genome and Radiation Stability Unit, Harwell, UK) where several of his students obtained their Ph.D. Degree using their pulse radiolysis facilities. It is through his efforts that the NCFRR is being established at the University of Pune.

Dr. T.S. Singh, after completing his Masters program in Physical Chemistry in 1996, obtained his Ph.D. Degree under Prof. B.S.M. Rao. His thesis work is concerned with pulse radiolysis studies of arenes and nucleobases. He is presently on the faculty, Department of Chemistry, University of Pune, pursuing his research in radiation chemistry.



Introduction

Radiation chemistry is the study of physical, chemical and biological reactions occurring as a result of the interaction of ionising radiation with matter. These radiations include not only high energy electromagnetic radiations such as X-rays and γ rays but also high energy charged particles such as electrons, protons, deuterons, α particles and accelerated heavy ions as well as neutrons.

Radiation research started in 1896 [1], 4 years prior to the Planck black body radiation theory and 17 years before the Bohr atomic model! The earliest researchers discovered that ionising radiation decomposes water [2], darkens glass, affects plants, and can be used for cancer treatment [3]. Later advances had to wait for future developments in other fields, e.g., the key genetic role of the DNA. Radiation research changed from a relatively restricted field to one of major importance after

World War II. The period from 1950-1970 was the 'golden age' of radiation research. New radiation sources were available for research applications including the nuclear reactor, ^{60}Co irradiator, and the microwave LINAC. Important discoveries made in this period include the mechanism of water radiolysis, identification of the hydrated electron and many other reactive free radicals and modification in the properties of polymers due to exposure to radiation and the role of DNA in radiation biology.

With the advent of new generation laser driven accelerators, the study of ultrafast phenomena is now possible and the early radiation chemistry events can be explored. It is believed that under this scenario, radiation chemistry will continue to grow and contribute not only in the area of chemistry but also in biology and physics.

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Radiolysis of Water

The radiation chemistry of water has been studied since the discovery of natural radioactivity. Water is the most important and abundant constituent of living matter. Also large amount of water are used as coolants in nuclear reactors. Therefore, radiation chemistry of water has been studied in great detail and water radiolysis now provides a convenient way of generating a host of unstable species under well-defined conditions.

The major products of water radiolysis are free radicals $\cdot\text{OH}$, e_{aq}^- , $\text{H}\cdot$, positive ions H_2O^+ and molecular products like H_2 and H_2O_2 . In the radiolysis of water almost equal amounts of reducing and oxidising radicals are produced. Therefore, methods had to be developed to study the individual reactions of these radicals by eliminating the remaining undesirable radicals.

A system containing almost 90% $\cdot\text{OH}$ radical can be obtained by saturating the aqueous solution with N_2O when the $\cdot\text{OH}$ radical gets converted into the hydrated electron as



The hydrated electron can also be scavenged by H_2O_2 to give the $\cdot\text{OH}$ radical

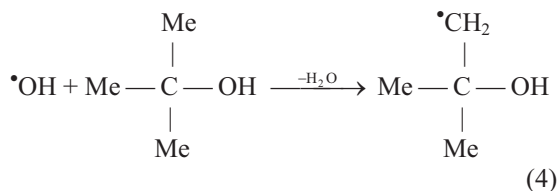


However, hydrogen peroxide reacts with the $\cdot\text{OH}$ radical and also the substrate radicals formed by the $\cdot\text{OH}$ attack.

The reactions of the H atoms can be studied under acidic conditions where the hydrated electron will be converted into H.



Although the $\cdot\text{OH}$ radical can be converted into e_{aq}^- , extreme conditions of pH and pressure of hydrogen (100 atm) are necessary. In order to avoid these extreme conditions, the $\cdot\text{OH}$ radical is scavenged by using tert-butyl alcohol because the resulting alcohol radical is unreactive towards most of the substrates and the primary radicals.

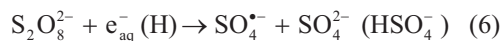


The primary radicals formed from the radiolysis of water can be converted into various secondary radicals like $\text{N}_3\cdot$, $\text{SO}_4^{\cdot-}$, $\text{Cl}_2^{\cdot-}$, $\text{Br}_2^{\cdot-}$ and $\text{I}_2^{\cdot-}$ and also several alkyl and aryl radicals.

The azide radical can be produced by irradiating N_2O saturated aqueous solution containing NaN_3 as shown



The sulphate radical anion ($\text{SO}_4^{\cdot-}$) can be produced by the reaction of the hydrated electron and H atom with $\text{K}_2\text{S}_2\text{O}_8$



Experimental Methodology

The techniques employed in the radiation chemical study are pulse radiolysis to monitor the transient species and the steady state radiolysis to determine the stable products formed.

Pulse Radiolysis

In a chemical reaction, the reactants give the products via a process in which many intermediate species are involved. Product distribution studies will give some information about the nature of these intermediates, but their identification and characterisation is possible if the reaction can be monitored over very short time intervals. This is indeed possible using the pulse radiolysis technique. In this method, reaction intermediates such as electrons, ions, radicals, and excited molecules are produced in high concentration by irradiation with pulsed high energy beams with very short pulse widths. A schematic diagram of a pulse radiolysis facility is shown in Fig. 1. The pulsed electron beam irradiates a flowing solution of the chemical. With a delay pulse generator, a flash of light is generated by a Xenon flash lamp and a shutter is opened for light to fall on the solution. The transmitted light, after being dispersed by a monochromator falls on a photomultiplier tube and the absorption as a function

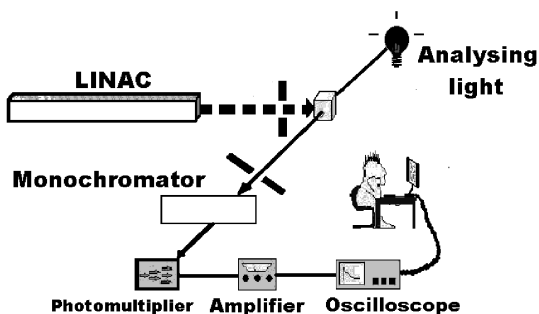


Fig. 1 Schematic diagram of a pulse radiolysis facility

of wavelength is recorded on a storage oscilloscope as well as the data are collected on a computer.

The time resolution of the equipment must be very short in order to study the kinetics of the radiation induced reactions because these reactions, in general, involve free radical and hence are very fast. Generally, electron pulses of a few nanoseconds are used. The laser driven next generation electron accelerators in pico and sub picosecond time range are either in operation or underway at the Brookhaven and Argonne National Laboratories in the U.S.A., Osaka and Tokyo Universities in Japan and at Orsay in France. The decay and the buildup of the intermediates and the stable products formed after the electron pulse can be monitored by various detection techniques.

Optical absorption is the most extensively used detection technique and is based on the difference in the optical absorption spectra of the starting material and the transients or products. The absorbance of the transient species at different wavelengths is obtained by scanning with a monochromator. Data storage and analysis are done using computers. A drawback of this technique is that, from the measured absorbance, only the product G_E is obtained and therefore, it is necessary to know the molar absorptivity of the intermediates or products from other studies to evaluate quantitatively the yields.

In the radiolysis of aqueous solutions, in addition to charged reactants (e_{aq}^- , H^+ , OH^-), charged intermediates or products may also be formed. Such

reactions can be monitored by measuring the differences in equivalent conductivity of various charged species following the pulse. This method is useful in elucidating the characteristics of the intermediates which cannot be detected by absorbance measurement.

Kinetics in Pulse radiolysis

In radiation chemistry, experimental conditions can be chosen so that the formation of a particular transient species can be studied exclusively. In pulse radiolysis, generally, the concentration of the reactants is kept higher than the other so as to obtain pseudo first order kinetics. The concentration of the radicals produced in radiolysis is of the order of 10^{-6} mol dm $^{-3}$ and the solute concentration is kept several orders of magnitude high. The reaction can be represented by the following expression,

$$-d[R^{\bullet}]/dt = k[R^{\bullet}][S] \quad (7)$$

The kinetics of the reaction can be studied by monitoring either the decay in the case of the hydrated electron or the growth of product formed as a result of the reaction. Whether the primary radical is undergoing reaction with the solute and not with self or any impurity present can be verified by varying the concentration of the solute. The pseudo first order rate constant will be directly proportional to the solute concentration.

Competition Method

When neither the primary nor the reaction product can be observed directly, the rate constant can be measured by a competition method using a scavenger. The scavenger basically competes with the solute and forms a product which can be monitored suitably. Consider the reaction of the solute S with the radical R^{\bullet} with a rate constant k_1 leading to the product P_1 and the reaction cannot be monitored by following P_1 or R^{\bullet} . If a scavenger Q is used to compete giving rise to product P_2 , which can be monitored,



the yield of P_2 can be given as

$$G(P_2) = k_2[Q]G_{R^{\bullet}} / (k_2[Q] + k_1[S]) \quad (9)$$

which can be rearranged to

$$G_{R\bullet}/G(P_2) = 1 + (k_2[Q] / k_1[S]) \quad (10)$$

The slope of the plot of $G_{R\bullet}/G(P_2)$ versus $[Q]/[S]$ gives the ratio k_2/k_1 . From the knowledge of k_2 the value of k_1 can be evaluated.

Steady State Radiolysis

More information on the mechanistic details of the reactions of free radicals generated by radiolysis with the compound of interest is obtained by the product distribution studies. The samples are irradiated for a sufficient period of time to ensure that all radical-radical and radical-molecular reactions are completed. Care has to be taken to keep the dose below a certain value to avoid secondary reactions. The stable products are characterised and determined quantitatively by various analytical methods.

Research Facilities for Study of Fast Reactions in Chemistry

Chemistry deals with the breaking and making of bonds. In the past, one knew what happened 'before' and 'after' a chemical change because the probes available were slow compared to the speed of a chemical reaction. Since the last three decades, the faster processes were being studied in the laboratory, thanks to the advent of electron accelerators which can provide pulses of high energy electron beam on a time scale of nano-seconds and lasers which can produce pulses of intense radiation in the femto-, pico- and nano-second regime. Thus, it is now possible to detect and characterise the transients in a chemical reaction. The smallest time scale in which chemical processes can now be time resolved has reached a value of sub-picosecond scale. Thus, the chemists have a tool to study the fast reactions. Some of the international and national laboratories using the pulse radiolysis facility are listed below.

National Status

In India there are a few groups involved in this type of work notably in BARC under the leadership of Dr. J. P. Mittal where both laser flash photolysis and pulse radiolysis facilities exist. The radiation group at the Department of Chemistry, University of Pune has an active collaboration program with

International Status

Canada	1. Pulse Radiolysis and Laser Flash Photolysis Facilities at Concordia University
Denmark	1. Riso National Laboratory, Riso
France	1. CEA-Saclay 2. Universite Paris-Sud, Orsay
Germany	1. HMI, Berlin 2. Max Planck Abteilung, University of Leipzig
Italy	1. Instituti di Fotochemi (High Energy Radiation Chemistry), Bologna
Japan	1. Hokaido University 2. Osaka University 3. Tokyo University 4. Waseda University
New Zealand	1. Auckland University, Auckland
Sweden	1. Swedish Royal Institute of Technology, Stockholm
United Kingdom	1. Gray Research Laboratory, Middlesex 2. Medical Research Council, Harwell 3. SRS, Daresbury
U.S.A.	1. Argonne National Laboratory 2. Brookhaven National Laboratory 3. NIST, Gaithersburg 4. University of Notre Dame

Bhabha Atomic Research Centre (BARC) and has extensively used the LINAC at BARC. In addition, there are several young researchers working in Indian universities and Institutes trained in radiation chemical research from within the country and outside who require to use the pulse radiolysis facility in their research work. However, due to the heavy load on the LINAC from within BARC, it has not been possible to cater to the needs of a large number of researchers from outside. The Board of Research in Nuclear Sciences (BRNS) has, therefore, approved our proposal for setting up of the National Centre for Free Radical Research (NCFRR) housing a LINAC for pulse radiolysis study.

TABLE 1. Specification of the LINAC

Parameter	Specification
Electron beam energy	7 MeV
Peak beam current @ 10 ns	1 A
Peak beam current @ 3 μ s	0.115 A
Beam diameter at exit window	2 mm
Jitter in pulse	± 200 ps
Pulse rate (Mains locked option)	50 to 200 pps in 12.5 pps steps
Radiation dose	0.1 to 100 krad / pulse
Dose due to dark current	< 1% of Beam current
Pulse to pulse reproducibility	$\pm 1\%$
Energy spread	± 0.5 MeV
Exit window material	Titanium
Single shot and multiple shots	50 to 200 pps
Preset beam pulses	10 to 250 pulses in steps of 10 pulses
Pulse width - 10ns to 3 μ s	10, 20, 50, 100, 200, 400 ns & 3 μ s

Linear Accelerator at the NCFRR

The specifications of proposed linear accelerator at the NCFRR for pulsed radiolysis are given in Table 1. The main features are: Electron energy 7 MeV, peak beam current 1 A, pulse width 10 ns, pulse repetition rate 10 to 500 per second and radiation dose 1 to 100 krad/pulse.

Applications

Radiation chemistry has contributed not only to chemistry but also to physics, materials processing, biology and medicine. The studies of the chemical aspects of radiation biology, solvation and electron transfer reactions, free radical chemistry of fullerenes, oxidative degradation of pollutants in water and studies on the catalytic mechanisms in zeolites have proved that radiation chemical techniques can be an important tool for chemists and biologists. Due to the constraint of space and multitude of applications, only work carried out in our group has been briefly discussed in this article.

Radiation Induced DNA Damage

The most important effect of radiation on the living cell is damage to the chromosome where the critical damage is that to the deoxyribose nucleic

acid (DNA) component of the chromosome. The studies of the radiation chemistry of DNA and its components resulted in a better understanding of the chemical modifications induced in DNA by ionising radiation.

The OH radical induced charge transfer between DNA nucleobases were studied. With the exception of dApdG, there was no significant evidence [4] for charge transfer between the OH adducts of the nucleobases and the parent nucleotide. Redox reactions of OH adducts of nucleosides with nitroaromatics and oxidants were also studied [5].

Radiation Chemistry of Substituted Benzenes

The radiation chemical oxidation of benzene and its monosubstituted derivatives by the OH radical has been widely studied. The pulse radiolysis technique combined with product distribution studies under steady state conditions has provided valuable information on reactivities, spectral nature of the intermediates and the redox chemistry of OH adducts of benzene and its derivatives.

The main reaction pathway for the \bullet OH reaction with benzene is by its addition to the ring leading to the formation of hydroxycyclohexadienyl radicals. The H abstraction is a competing reaction

with derivatives containing groups like NH_2 , OH , or CH_3 , the extent of this reaction being dependent on the substituent. Because of the acidic nature of H in NH_2 , aniline undergoes the H abstraction reaction to give anilino radical more readily when compared to phenol or toluene to generate the phenoxyl or benzyl radical. We have reported [6-14] the radiation chemical oxidation of disubstituted benzenes of the type $\text{C}_6\text{H}_{5-n}\text{X}_n\text{Y}$, where X is a halogen and $\text{Y} = \text{Cl}$, Br , CH_3 , CH_2Cl , CF_3 or OCH_3 . Furthermore, with chlorotoluenes and cresols, the extent of the $\cdot\text{OH}$ attack at each position was estimated by steady state studies.

Azo Dyes

Azo dyes have a wide variety of applications in the textile, paper, food and pharmaceutical industries. The oxidation and reduction of azo dyes and its ortho and para methoxy, chloro and methyl derivatives initiated by radicals generated by pulse radiolysis were investigated. An understanding of these processes gave an insight into the reaction pathways leading to decolorisation of the dyes [14].

Ruthenium Complexes

The work on the reactions of oxidizing ($\cdot\text{OH}$ and $\text{N}_3\cdot$) and reducing (e_{aq}^-) radicals with the ruthenium compounds complexed with 1,10-phenanthraline and quinoxaline ligands is undertaken at our laboratory to obtain an insight into the redox chemistry of these complexes.

References

1. H. Becquerel, *Compt. Rend.*, 1896.
2. W. Ramsay, *J. Chem. Soc.*, **91** (1907) 931.
3. E. H. Grubbé, *Radiology*, **21** (1933) 156.
4. M. M. M. Bamatraf, P. O'Neill and B. S. M. Rao, *J. Phys. Chem. B*, **104** (2000) 636.
5. M. M. M. Bamatraf, P. O'Neill and B. S. M. Rao, *J. Am. Chem. Soc.*, **120** (1998) 11852.
6. H. Mohan, M. Mudaliar, C. T. Aravindakumar, B. S. M. Rao and J. P. Mittal, *Radiat. Phys. Chem.*, **40** (1992) 513.
7. H. Mohan, M. Mudaliar, C. T. Aravindakumar, B. S. M. Rao and J. P. Mittal, *J. Chem. Soc., Faraday Trans. 2* (1991) 1387.
8. G. Merga, C. T. Aravindakumar, H. Mohan, B. S. M. Rao and J. P. Mittal, *J. Chem. Soc., Faraday Trans.*, **90** (1994) 597.
9. G. Merga, H. Mohan, B. S. M. Rao and J. P. Mittal, *J. Phys. Chem.*, **98** (1994) 9158.
10. S. C. Choure, M. M. M. Bamatraf, B. S. M. Rao, H. Mohan, J. P. Mittal and R. Das, *J. Phys. Chem. A*, **101** (1997) 9837.
11. S. B. Sharma, B. S. M. Rao, H. Mohan and J. P. Mittal, *J. Phys. Chem. A* **101** (1997) 8402.
12. T. S. Singh, S. P. Gejji, B. S. M. Rao, H. Mohan and J. P. Mittal, *J. Chem. Soc., Perkin Trans 2* (2001) 1205.
13. S. Geeta, S. B. Sharma, B. S. M. Rao, H. Mohan, S. Dhanya and J. P. Mittal, *J. Photochem. Photobiol. A: Chem.*, **140** (2001) 99.
14. K. K. Sharma, B. S. M. Rao, H. Mohan, J. P. Mittal, J. Oakes and P. O'Neill, *J. Phys. Chem.*, **106** (2002) 2915.

CdTe nanoparticles Dispersed in Glass Thin Films grown by Magnetron Sputtering Technique



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Abstract

In this article the results of the size dependent structural, optical and compositional characterization of CdTe nanoparticles in SiO₂ thin films have been summarized. It has been demonstrated that using the present technique of magnetron sputtering, size and surface structure of the CdTe nanoparticles can be tailored by controlling the deposition parameters. This work has been carried out as a project sponsored by Board of Research in Nuclear Sciences at Thin Film Laboratory, Indian Institute of Technology, Delhi in

collaboration with Light Scattering Group at Indira Gandhi Centre for Atomic Research, Kalpakkam.

Introduction

Semiconductor nanoparticles dispersed in optically transparent glass thin films have emerged as a new and exciting nanomaterials system. Since the first experimental demonstration of degenerate four wave mixing, large non-linearities with sub-nanosecond recovery times and high optical gain in CdS_xSe_{1-x}, semiconductor dispersed glasses have evolved as potential candidates for linear and

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non-linear optical devices [1-2]. Recently a net optical gain has been observed in Si nanoparticles dispersed in SiO₂ matrix [2]. The optical bi-stability along with the relaxation time of the order of picoseconds has made these glasses suitable for optical computer applications [3].

Semiconductor nanoparticles dispersed in glasses are popularly known as semiconductor doped glasses (SDG). In addition to the above applications, the worldwide research activity towards synthesizing these materials is also aimed to understanding the basic physics in the low dimensional structures [4-9]. A complete protection of surface structure of the nanoparticles in an inorganic dielectric matrix is one of the advantages of SDG in comparison to chemically capped or nanoparticles dispersed in polymeric materials. SiO₂ matrix protects nanoparticles in early stages of growth as well as during post deposition studies, characterization and device operation. The objective of this article is the results of the structural, optical and compositional investigations carried out on CdTe nanoparticles dispersed in SiO₂ thin films.

In the present study CdTe nanoparticles dispersed in SiO₂ films have been grown by rf magnetron sputtering technique. This technique to

prepare semiconductor nanoparticles seems to be superior in comparison to other methods reported in the literature [10-12], since the size of the dopants can be controlled by the relative surface area or positioning the semiconductor chips on the silica target. The advantageous of rf magnetron sputtering have been described elsewhere [12].

In most of the studies reported on the synthesis of SDG using magnetron sputtering technique, CdS and CdTe compound targets along with SiO₂ target have been used. The composition of semiconductor depend on the sputtering conditions and post deposition annealing parameters and it was not possible to vary the composition without effecting the size, structure and nanoparticle concentration. This problem has been circumvented by using elemental Cd and Te targets along with SiO₂ target. Effect of thermal annealing conditions on the structure of the surface layer and the nanoparticle core has been studied using glancing angle X-ray diffraction, x-ray photoelectron spectroscopy and transmission electron microscopy techniques.

Deposition Technique

A schematic diagram of the deposition set up is shown in the Fig. 1. It consists of a Rotary Vane

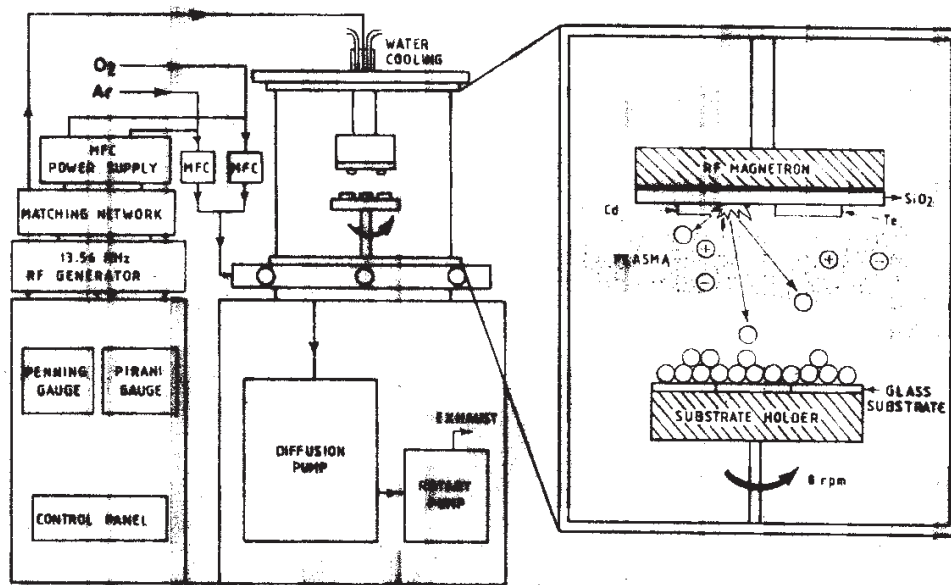


Fig. 1 Schematic diagram of the rf magnetron sputtering system.

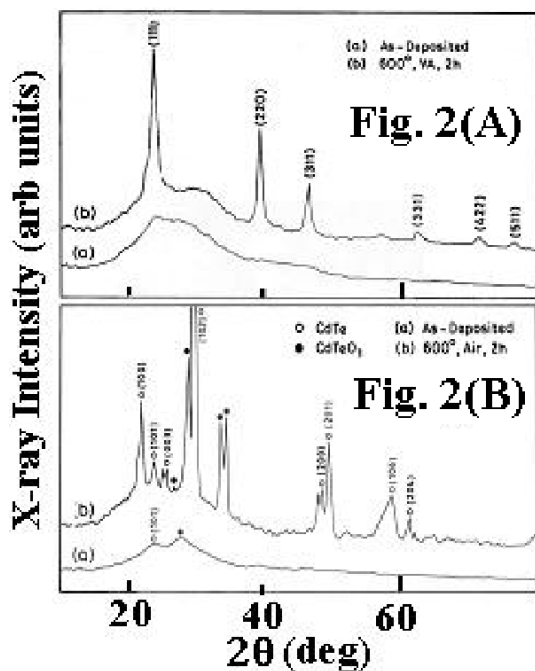


Fig. 2 X-ray diffractogram of CdTe:SiO₂ samples annealed in (A) Vacuum (B) Air at 600°C

Pump (LEYBOLD-HERAEUS, Trivac-D16B, pumping speed 4.5 l/s or 275 l/m) coupled to oil Diffusion Pump (BOC- Edwards, Diffstak 100/700, pumping speed 700 l/s) for creating high vacuum. A cylindrical bell jar has been used as a vacuum chamber where sputter gun (TOROUS 2C, Kurt J LESKER Company, USA) has been positioned over the substrate area. The well-polished base plate has feed throughs for gas connections, electrical connections, air inlet valve etc. The sputter gun has a planar (circular) permanent magnet (575 Gauss) to confine the plasma. Below the magnet a copper groove has been designed for fixing the target. The target assembly is under cooling during sputtering. The substrate holder can be moved vertically to maintain the required electrode separation. A shutter has been arranged in between two electrodes to prevent contamination from the target reaching substrates during sputter cleaning. RF generator (CX 600/13.6 MHz, COMDEL, USA) has been connected to the sputter gun through the matching network (COMDEL, CMM-1000) to transform maximum power from generator to the load. The

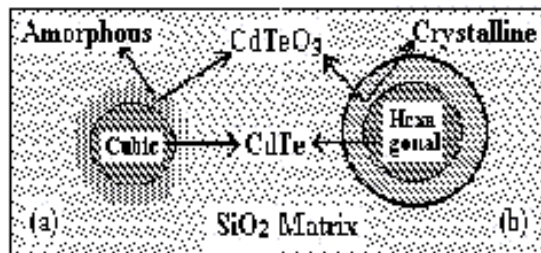


Fig. 3 Schematic diagram showing (a) CdTe nanoparticles having cubic structure surrounded by an amorphous CdTeO₃ interfacial layer and (b) CdTe nanoparticles having hexagonal structure capped by a crystalline CdTeO₃ layer.

substrate rotation (8 rpm speed) has been employed to maintain the uniformity of nanoparticles growth with uniform CdTe:SiO₂ composition through out the deposition area. The target consists of high quality Cd and Te discs symmetrically placed on the 2-inch diameter SiO₂ plate.

Results and Discussion

X-ray diffractograms in Fig. 2 shows that as-deposited (AD) films were amorphous in nature [13]. Post deposition heat treatment has been done in both vacuum and air ambients from 100 to 600°C. It has been observed that the structure of the nanoparticle can be controlled by varying the annealing environment. Vacuum Annealing (VA) [in Fig. 2(A)] leads to complete formation of cubic nanoparticle phase and air annealing (AA) [in Fig. 2(B)] leads to the formation of hexagonal nanoparticle phase. On annealing at 600°C in vacuum, diffusion of Cd and Te in SiO₂ matrix results in coalescence leading to the growth of CdTe nanoparticles having cubic structure with an amorphous CdTeO₃ interfacial layer. The schematic diagram showing the formation of an amorphous interfacial and crystalline capping layers around CdTe nanoparticles in VA and AA samples, respectively is shown in Fig. 3 (a, b). In VA samples, amorphous CdTeO₃ phase present around the CdTe nanoparticles is due to the interaction of oxygen atoms from the SiO₂ with Te at the nanoparticle-matrix interface. During annealing in air, diffusion of ambient oxygen through SiO₂ matrix

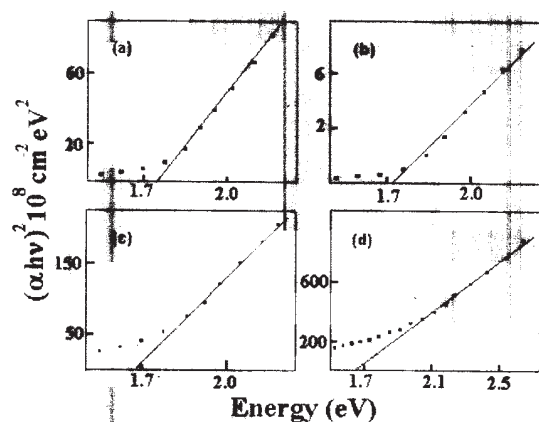


Fig. 4 Tauc plots showing the blue shift of optical absorption edge of CdTe:SiO₂ samples with respect to bulk CdTe: (a) AD, (b) VA at 200, (c) VA at 400 and (d) VA at 600°C.

takes place and the reaction of oxygen with CdTe at the nanoparticle surface is enhanced, resulting in the formation of a crystalline CdTeO₃ capping layer. Optical transmittance and reflectance analysis were carried out to study the size dependence of absorption edge in these samples. The results from the Tauc plots shown in Fig. 4 clearly shows a blue shift (≈ 0.25 eV) in optical absorption edge with respect to bulk CdTe and confirms the nanoparticle character of CdTe and this shift corresponds to the nanoparticle size of 4–5 nm [14].

TEM analysis shows the nanoparticle features having an average particle size of 6–8 nm [15]. Results of AFM studies carried out on AD and VA sample showing the growth of nanoparticles in the SiO₂ matrix is shown in Fig. 5. Results of XPS studies carried out on CdTe:SiO₂ samples are shown in the Fig. 6. The consistence occurrence of Si peak around 104 eV in Si 2P spectra from Fig 6(a) to 6(c) is a signature of presence of SiO₂ in the sputtered film. The absence of CdO peaks in Cd 3d_{5/2} and Cd 3d_{3/2} spectra from 6 (d) to 6(f) indicates that Cd is strongly bonded with Te. The splitting of Te 3d_{5/2} peak in 6(g) to 6(i) in both VA and AA samples shows the presence of CdTeO₃ phase in the form of a surface layer. Thus surface structure of the CdTe nanoparticles has been found to sensitively depend

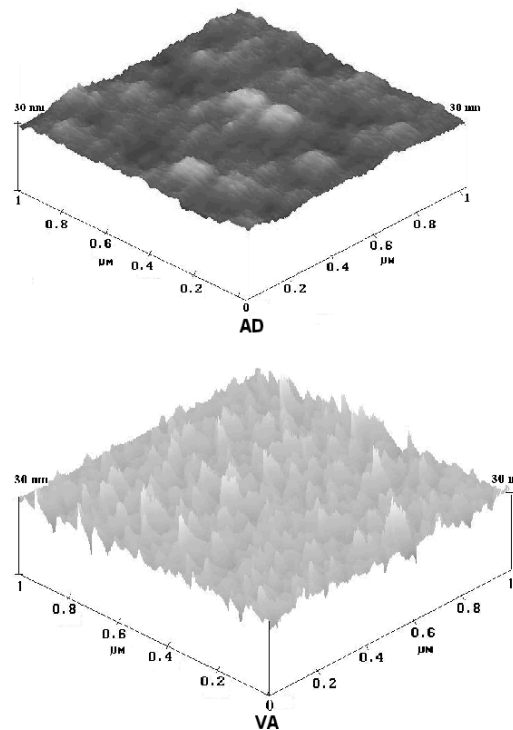


Fig. 5 AFM micrographs showing the growth of CdTe nanoparticles in the SiO₂ matrix, (a) AD and (b) VA samples.

on the annealing ambient. The crystalline CdTeO₃ capping layer in AA sample in place of an amorphous interfacial layer in VA samples, changed the CdTe structure from cubic to hexagonal. The structural differences between the CdTe and CdTeO₃ at the nanoparticle-oxide interface introduces a large concentration of stacking faults resulting into a surface mediated structural transformation. The mechanism of the structural transformation has been explained in the earlier publication [15].

Conclusions

In the present study, CdTe nanoparticles dispersed in SiO₂ thin films have been grown by magnetron sputtering technique. It has been successfully shown that, it is possible to control the nano particle concentration and composition by controlling the target composition and sputtering parameters. By controlling of post deposition

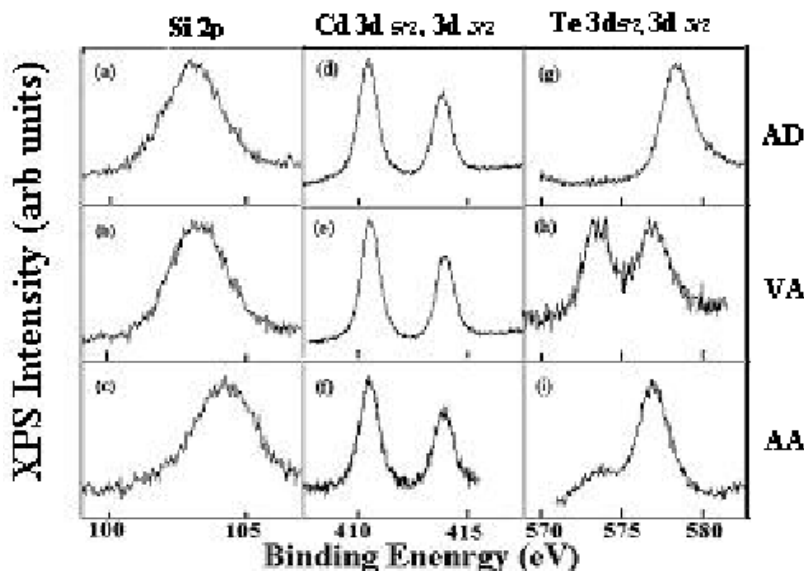


Fig. 6 XPS core level spectra (a-c) Cd $3d_{5/2}$ and Cd $3d_{3/2}$, (d-f) Te $3d_{5/2}$ and (g-i) Si $2p$ of CdTe:SiO₂ AD, VA and AA samples, respectively.

annealing ambient, it possible to control the surface structure of CdTe nanoparticles. A structural transformation from cubic to hexagonal phase mediated purely by surface effects have been reported for the first time in any nanoparticle system.

References

1. R.K. Jain and R.C. Lind, *J. Opt. Soc. Am.*, **73** (1983) 647.
2. Pavesi L, Dal Negro L, C. Mazzoleni, G. Franzo and F. Priolo, *Nature* **408** (2000) 441
3. J. Yumoto, S. Fukushima and K. Kubodera, *Opt. Lett.* **12** (1987) 832
4. L. E Brus, *J. Phys. Chem* **90** (1986) 2555
5. Y. Wang et al., *J. Phys. Chem.* **91** (1987) 257
6. M. A. Anderson et al., *J. Phys. Chem.*, **101** (1997) 5895
7. Al. L. Efros et al., *Sov. Phys. Semicond* **16** (1982) 772
8. A. I. Ekimov et al., *Sov. Phys. Semicond* **16** (1982) 775
9. B. G. Potter et al., *Phys. Rev. B.* **37** (1988) 10838
10. A.G. Rolo, O. Conde and M.J.M. Gomes, *Thin Solid Films* **318** (1998) 108
11. Keiji Tsunetomo, Hiroyuki Nasu, Haruyuki Kitama, Akira Kawabuchi, Yukio Osaka, and Ken Tkiyama *Jpn. J. Appl. Phys* **29** (1990) 2111
12. B.G. Potter Jr. and J.H. Simmons, *J. Appl. Phys.* **68** (1990) 1218
13. P. Babu Dayal and B.R. Mehta B R, Proc. International Work shop on Physics of Semiconductor Devices (IWPSD) 11-15 Dec-2001, IIT Delhi, Edited by Kumar V and Basu P K, Allied Publishers, New Delhi, India, Vol: 1, p. 343
14. P. Babu Dayal and B.R. Mehta (to be communicated)
15. P. Babu Dayal and B.R. Mehta, S.M. Shiva Prasad and Y. Aparna, *Appl. Phys. Lett.* (In press)

Thermal Ecological Studies in India: A DAE-BRNS Initiative



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Introduction

The prosperity of a nation can be judged from its per capita electric power consumption. Every kind of industrial development has its costs and benefits and electric power generation is no exception. The costs include both the financial burden as well as the ecological impact on the environment. In recent years, the appreciation for such ecological/environmental costs is, slowly but surely, increasing all over the world. Sustainable development in the power sector requires use of eco-friendly technologies which aim to keep the productivity high without compromising the environmental safety.

Electric power plants are often strategically located in the close proximity of natural water bodies such as lakes, rivers, estuaries and oceans. This is to enable them to make use of such water bodies as heat sinks. In addition to heat, power plant effluents produce significant mechanical turbulence and also release biocides (usually chlorine), trace metals, fly ash and low level radioactivity into the aquatic environment [1]. Amongst all these, the thermal discharge into water bodies is the major concern, both for power producers and especially for the

environmental regulatory agencies, such as the Ministry of Environment and Forestry (MOE&F) and Pollution Control Board (PCBs) in our country. Electric power production can lead to increase in temperatures in two distinct ways, namely (a) a direct discharge of heated water, and (b) indirect global warming through CO₂ and other green house gases (GHGs). Thermal power plants discharge heat into environment in both the aforesaid ways. In the case of nuclear power plants [2] dissipation of heat is only through the plant cooling water systems.

Whether thermal and other discharges from power plants, nuclear or otherwise, can affect the growth and distribution of life-forms living in aquatic environments needs serious consideration. Apart from the need for preservation of quality of the environment, a holistic understanding of the ecosystem is also necessary to find solutions to a variety of problems that crop up during plant operation. Some of the major problems relevant to our own nuclear power plants are large scale ingress of jelly fish and sea weeds, problems due to macrophytes in water reservoir, flow blockage due to macrofouling in intake systems, siltation of pump chambers and biofouling of condenser tubes [3]. Most of these problems are related either directly or

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indirectly to biological activity in the water bodies. Therefore, ecological survey of water bodies around power plants is an important endeavor from both the environmental and operational point of view.

Temperature Tolerance of Living Organisms

High temperatures are not entirely undesirable for life functions. In fact, most life forms of tropics generally show an optimum temperature requirement of 30°C-37°C for their growth and development. Life begins to be adversely affected at temperatures above 40°C. However, the diversity in the habit and habitat of living beings stretch these temperature tolerance limits in different regions of our planet [4]. For example, cryophiles and psychrophiles do not grow well above 15°C-20°C while the flora and fauna of hot springs can thrive well even at 70°C-80°C. Some of the microbes found in deep-sea vents even survive temperatures around 100°C and above. Thus, no uniform temperature tolerance range can be defined for the living world. However, most life forms (mesophiles) show an optimum temperature requirement in the range of 25°C-30°C. They also tolerate temperature rise up to 42°C, though temperatures above 45°C are generally lethal.

Why are Biological Activities thermosensitive?

The adverse effects of high temperature on biological systems can be looked at three different levels – namely at the level of molecules and cells, at the level of organisms and at the level of communities and ecosystems. Notwithstanding the wide variation in their temperature tolerance limits, the targets of heat sensitivity in all the life-forms are almost identical at the cellular and molecular level. These include denaturation, inactivation and degradation of biomolecules, especially proteins, which slow down the cellular metabolism and eventually bring the growth to a halt. Most life-forms are equipped to deal with the impairments caused by moderate temperature upshifts (ΔT of 5°C-15°C) of short durations (from minutes to a few hours). This is facilitated by invoking the so-called heat shock response, wherein novel proteins, termed the heat-shock proteins, are synthesised within minutes of temperature upshift [5]. This is brought about by activation of expression of heat-shock genes. The heat-shock response, including the various genes

and proteins, is a universal response conserved among all living forms from bacteria to plants to animals, including man. Equipped with the heat-shock response, most mesophilic organisms can efficiently handle short-term temperature upshifts within reasonable limits. The heat-damaged protein molecules are either repaired or discarded/degraded with the help of heat-shock proteins and normalcy is restored to cells.

Thermal Response of Organisms and Ecosystems

Unfortunately, due to several reasons, cellular tolerance/sensitivity to rise in temperature does not always reflect the tolerance/sensitivity at the level of organisms or ecosystems. Individually many life-forms, such as bacteria, algae, fungi, insects, plants and animals have been investigated in laboratories for their tolerance to high temperatures. But such “knowledge” based on a few model organisms does not allow us to predict the thermal behavior of other “similar” organisms. Some of the measurable results can at times be misleading, for example, a thermosensitive motile form can simply avoid thermal stress (by moving away from it and returning when optimal temperatures are restored) and be rated as thermotolerant. There are developmental stages in an organism’s life which may be more or less thermosensitive than the organism itself. Temperatures even determine the sex of certain reptiles like crocodiles. Above all, the information based on individual organisms can not be extrapolated to ecosystems since they tend to be highly heterogeneous, location-specific and subject to seasonal variation. Also the intricate relationships between different organisms in a food chain complicate prediction of thermal response of ecosystems.

Thermal tolerance spectrum of aquatic organisms is much lower than that of terrestrial life-forms. Thermal discharge into water bodies can, therefore, affect the aquatic ecosystem constitution due to close-knit interactions between different ecosystem components. Such changes may vary from subtle to significant. Some of the well-established “ill effects” of thermal pollution in aquatic systems include (a) loss of economically important life-forms, (b) changes at the level of primary producers (diatoms to green algae to cyanobacteria), (c) reduction in ecosystem

productivity (which in turn affects the entire food chain), and (d) loss of certain habitats such as the coral reefs [6]. Coral reefs, which provide shelter to nearly 25% of all the marine life-forms tolerate a rather narrow temperature range of 25°C-29°C and are known to “bleach” upon temperature rise above 32°C. Coral bleaching and consequent loss of the entire dependent communities is the best documented example of serious loss of biodiversity in response to ocean warming in recent years. Thermal pollution may also cause the rise of opportunists (pathogens, biofoulants, algal blooms etc). Elevated temperatures also cause depletion of dissolved oxygen which, coupled with higher oxygen demand at elevated temperatures, results in considerable stress on all living organisms in aquatic ecosystems.

Notwithstanding the aforesaid ill effects, the experience in temperate climates has shown little ecological effect due to heated effluent discharge. Thermal pollution of water bodies does not seem to be a cause of serious concern in those areas [2,6]. Tropical organisms live at temperatures closer to their upper limits of tolerance, as compared to their temperate counterparts and can be expected to be more sensitive to ΔT . As mentioned earlier, mesophiles abound the water bodies that act as sinks for thermal discharges from power plants in tropics. *A priori* it would, therefore, appear that given a ΔT of 5°C-15°C that does not increase the temperature of the water body above 40°C, most organisms in tropical water bodies should not face any serious threat from thermal discharges *per se*. But when they co-exist as a food chain in an ecosystem how do they respond to temperature upshifts has been rarely studied. For our country such thermotolerance data at the level of ecosystems do not exist. In view of this, it would be premature to predict the thermal behaviour of an entire aquatic ecosystem based on data on thermotolerance of a few individual mesophiles.

The need for Thermal Ecological Studies

To discuss various aspects of thermal ecology related to heated water effluent discharge from power plants, Dr. K.V. K. Nair - a pioneer in thermal ecological studies in this country, organised a discussion meeting at Kalpakkam in August, 1997. In

addition to ecological researchers in the country, the meeting was attended by participants from power sector as well as representatives from MOE&F and CPCB. At this meeting the need to obtain *in situ* data on the biological impact of temperature rise due to thermal discharges in the vicinity of electric power generation units was strongly emphasised. The major El Nino/ocean warming experiences in the subsequent year (1998) clearly demonstrated the ill effects of thermal pollution on large-scale bleaching of coral reefs. Alarmed by this, the thermal pollution related guidelines underwent a major revision in many parts of the world in 1998, including India.

The 1998 pollution control legislation from MOE&F (Table 1), which stipulates that condenser effluents should not have a temperature greater than 5°C above the intake water, created a serious problem for power plant operators. The plants that were in operation then, and even now, have been generally designed for a ΔT of 10°C across the condenser. Enforcement of the new ΔT limits would necessitate the new plants to go for bigger condensers or cooling towers adding significantly to the rising costs. There was no evidence of any adverse biological impact from the operating experience of the power plants due to discharge of heated effluents. Furthermore the rationale behind the new 5°C limit was not explained in the new legislation. Although it appeared to be an arbitrary extrapolation of regulatory guidelines from one region of the globe to another, in the absence of any data for Indian sites, such “over-cautious” approach of the regulatory agencies seemed ecologically justified.

The new standards for thermal discharge specified by MOE&F have important implications, both for the existing and in particular the forthcoming power plants in the country, both nuclear and thermal. Unless proven to be justified, these stipulations can turn out to be very expensive and counter-productive for the power industry. All this calls for extensive investigations on the response of aquatic life to elevated temperatures so that appropriate guidelines on limits could be evolved based on scientific framework.

TABLE 1. Standards for thermal discharge from power plants

(Gazette of India Notification G.J.R.7 dated 22.12.1998)

<p>Temperature Limit for Discharge of Condenser Cooling Water from thermal Power Plants :</p> <ol style="list-style-type: none"> 1. New plants commissioned after June 1, 1999 and using waters from rivers/lakes/reservoirs shall install cooling towers irrespective of location and capacity 2. New plants in coastal areas using sea water should adopt suitable system to reduce water temperature at the final discharge point, so that the resultant rise in temperature of receiving water does not exceed 7°C over and above the ambient temperature of receiving bodies. <p>For existing power plants the rise in temperature from inlet to the outlet of the condenser shall not exceed 10°C.</p>
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The DAE-BRNS CRP on TES : Objectives and Work Plan

In order to make a realistic assessment of biological impact of thermal discharge, it is necessary to obtain in situ data on the flora and fauna prevalent in the vicinity of the existing and forthcoming power plants. With this in view, DAE took the initiative in setting up the first major thermal ecological study (TES) in the country sponsored by the Board of Research in Nuclear Sciences (BRNS) in 1999. A co-ordinated research project (CRP) to investigate the thermal ecology of the environment around two of its existing (Kalpakkam and Kaiga) and one forthcoming (Kudankulam) nuclear power plants was set up and funded by BRNS (Table 2) [7]. A total of 8 laboratories from different universities/institutes are participating in this effort which is co-ordinated and monitored regularly by an expert committee (CMC-TES). At Kudankulam the effort seeks baseline ecological information about the site while at Kalpakkam and Kaiga the major aim

TABLE 2. DAE-BRNS CRP on Thermal Ecological Studies

<p>Nodal laboratories, Co-ordinators and Principal Investigators</p> <p>WSCL, KALPAKKAM : Dr. S. Narasimhan</p> <ol style="list-style-type: none"> 1. Prof. N. Sukumaran, SPKCES, Alwarkurichi Baseline studies on thermal ecology of Kudankulam marine environment 2. Prof. Shahul Hameed, J.M. College, Trichy A study on water quality and littoral benthos for impact assessment in the vicinity of MAPS thermal outfall 3. Prof. V.N. Raja Rao, University of Madras Impact of heated water effluent from a coastal power plant on microalgae 4. Prof. S. Jayachandran, University of Pondicherry Microbial ecology in the vicinity of a coastal atomic power plant 5. Prof. T. Subramoniam, University of Madras Distribution and behavioral patterns of the mole crab in the vicinity of MAPS thermal outfall <p>ESL, KAIGA : Dr. P. M. Ravi</p> <ol style="list-style-type: none"> 6. Dr. T.K. Ghosh, NEERI, Nagpur Baseline aquatic ecology of Kadra reservoir, the source of cooling water for Kaiga nuclear power plant 7. Dr. M.N. Madhyastha, Mangalore University Baseline studies on benthic ecology and thermal tolerance of some selected species from Kaiga environs 8. Dr. S. Ayyappan, CIFE, Mumbai Thermal tolerance of important fish species from Kali river, Karnataka
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is to assess the effects of thermal discharge, if any. The project has the following specific objectives :

1. Survey of the physico-chemical parameters of water quality, nutrient status and occurrence and distribution of major flora and fauna around the Kudankulam site

TABLE 3. What is being done under the CRP on TES?

Information	Kalpakkam	Kudankularm	Kaiga
Number of PIs	4 + 1	1	4
Study area	3 km x 500 m DP	1 km radius SC	1 km from DP
Sampling points	15		
Cruises	<pmtj;u		
Temperature	24°C-32°C	24°C-30°C	26°C-30°C
$\Delta T^{\circ}C$	7°C-10°C	--	6°C-8°C
Chemical quality	✓	✓	✓
Nutrients	✓	✓	✓
Bacteria	✓	--	✓
Algae	✓	✓	✓
Phytoplankton	✓	✓	✓
Zooplankton	✓	✓	✓
Fungi	--	--	✓
Benthic forms	✓	✓	✓
Fishes	✓	✓	✓
Carbs	✓	✓	--

2. Measurement of thermal plume and its distribution around and away from the discharge point at Kalpakkam and Kaiga
3. Evaluation of the effect of thermal discharge on the water quality and nutrient status
4. Assessment of the biological impact of thermal discharge in the vicinity of power plants in operation.

At all the three sites, data collection has been planned over a three year period to cover possible seasonal variations in the parameters under study. Data are collected through regular monthly cruises conducted over a fairly large area. To make comparisons relevant and meaningful data on all aspects are collected through the same cruise at each site. The sampling sites have been carefully chosen to make the data representative for the given site. Sampling reproducibility has been ensured by fixing

the sampling sites with the help of GPS and buoys. Samples collected from each cruise are immediately processed and analysed at the study site itself and also taken to the individual laboratories for further long term analysis. Collection and analysis of all data are carried out using internationally accepted techniques and standard instruments.

Major data collected in each cruise (Table 3) include temperature profiles, physico-chemical parameters of water quality and occurrence and distribution of various biological forms [7]. The thermal plume distribution is being studied at Kalpakkam and Kaiga in all the three dimensions. Apart from regular parameters (pH, salinity, suspended matter, BOD etc), water quality analysis pays special attention to nutrient status (nitrate, phosphate and trace elements) and occurrence of pathogens (such as coliforms). The biota are being examined at all trophic levels, viz. primary

producers (phytoplankton, algae, cyanobacteria), consumers (zooplankton, insects, molluscs, crabs and fishes) and decomposers (bacteria and fungi). Special attention is being paid to the benthic flora and fauna since these forms, on account of their non-motility, have to really endure various environmental stresses. Fish catch is also being monitored to assess the economic impact of thermal discharge. Study of the entire ecosystem involving all representative food chain constituents is a special feature of the CRP, not attempted in India earlier.

Novel Features Investigated under the CRP on TES

Experiments under the CRP have been designed to address issues relevant to stipulations/guidelines prescribed by MOE&F for existing/new power plants. An inland fresh-water site (Kaiga) has been included in the study along with a coastal (Kalpakkam) plant site. The thermal discharge from power plants can not be considered as a “point discharge”. In fact it can take the shape and form of a small pipeline to a long canal. Also the sink can vary from a vast ocean to a lake, a reservoir or a river. It would be more practical, therefore, to consider and evolve the idea of a “mixing zone” instead, where (a) heated effluent discharges can be allowed to mix with the water body, and (b) beyond the limits of which the life-forms would be safe from possible ill effects of thermal discharges, if any. Again in the absence of data on these aspects it is difficult to describe the dimensions of a mixing zone. To determine this, a careful assessment of all the parameters is being carried out under the present CRP at the discharge point and through a linear distance of over a kilometer and in a radius of 500m. When compared with similar data from the intake point and other control points in the respective water bodies, these analyses would yield a realistic estimate of the physical limits of a mixing zone, safe from both thermal as well as biological points of view.

Validation of the field data and the conclusions derived therefrom by appropriate laboratory studies is an integral part of the present CRP. In particular, the observed biological effects of the thermal discharge are proposed to be tested again in the laboratories. For this, the representative dominant species from each trophic level at each site

(including Kudankulam) will be subjected to ΔT of 5°C, 7°C or 10°C and their effects on the growth, metabolism, development, behavior and reproduction will be examined under conditions which simulate their *in situ* environs. These studies will enable identification of features which determine the observed field distribution of these species. They will also reveal the individual sensitivities/tolerances of different trophic levels and allow interpretations of the observed total effect on the entire ecosystem. It should be emphasised that while the guidelines for thermal discharge concern only the ΔT effects, the study plan is designed to identify the temporal (seasonal) and spatial effects also and distinguish them from thermal effects. The study will also identify site-specific unique features, if any, and allow predictions on ΔT effects for the Kudankulam site. These can subsequently be verified by another independent study after commencement of power plant operation.

The project attempts to obtain a comprehensive picture of different aspects of thermal ecology in the vicinity of two pre-existing nuclear power plants and also Kudankulam, the site of a proposed nuclear power plant in future. While the studies at Kalpakkam and Kaiga would assess the biological impact of thermal discharge from the operation of these plants, those at Kudankulam would help to obtain valuable baseline information that would be of immense use in future post-operational assessment of biological impacts at this site. Both at Kalpakkam and at Kaiga, the additional power generation units have been proposed and so the data obtained for these sites now would also serve as the baseline data for the new power units. When completed in a year from now, the project is expected to bring forth information on major issues that relate to the guidelines for thermal discharge, both current and newly proposed, stipulated by MOE&F.

Co-ordination and Monitoring of the CRP on TES

The BRNS-CRP on Thermal Ecological Studies (TES) began in April, 2000. The projects were subjected to a lot of discussion and careful critical evaluation aimed at making their outcome as relevant and meaningful as possible. The studies are being pursued with active research contributions

from 8 Principle Investigators (PIs) from reputed universities and national research institutes in a collaborative mode with the Water and Steam Chemistry Laboratory (WSCL), Kalpakkam and Environmental Survey Laboratory (ESL), Kaiga which act as the nodal agencies. Participation of universities and non-DAE institutes from geographical regions under consideration, helps address local environmental concerns and generates unbiased data. The project is being effectively co-ordinated and monitored by a Co-ordination and Monitoring Committee (CMC) comprising experts from BARC, NPC, NIOT, NIO, OPMEC-CECRI and MOE&F. This helps in the improvisation of approaches, applying mid-course corrections and focussing and re-focussing the objectives of the study. It also enables the project to be appropriately oriented to address concerns and requirements of both the power producers and regulatory agencies aided by ecological experts.

The project operates in an interactive mode between the PIs and the CMC-TES and is being continuously evolved with help and inputs received from various sources from time to time. The multidisciplinary expertise available under the CRP is being coupled to seek data, even more superior than originally envisaged. For example, in the last year of the project an exercise in modeling of the thermal plume emanating from heated water discharge, not envisaged originally, has been undertaken at Kaiga. A mathematical model for this freshwater site has been prepared and is now being validated by actual experimentation.. This will enable prediction of the thermal plume distribution in a site-specific way and possibly also forecast the magnitude as well as the effect of additional thermal discharge from units proposed to be added at this site in near future. The possibility of including the Geographical Information Service-Remote Sensitivity (GIS-RS) approaches for temperature measurements is also being actively considered for Kalpakkam site to seek additional validation of the ground observations that will be physically made by the investigators.

What has the Study Revealed so far?

After 2 years of well-planned studies under the CRP, some trends are already available [7]. Careful monitoring of thermal plumes at Kalpakkam and

Kaiga show that these plants have been operating in total compliance with the MOE&F stipulations. The ΔT values at both sites reduce to less than 5°C at the surface within a few hundred meters from the outfall and in less than 3 meters of depth. Thermal discharges at Kaiga and Kalpakkam also do not have any significant effect on the water quality and nutrient status. Clear indications are also available on the biological impact of the heated water effluents at Kalpakkam and Kaiga. At both the sites, the general abundance of biota decreases at the outfall but is restored to near normal within a short distance from the discharge point. It is expected that such data would help to clearly define a "mixing zone".

In the final year, plans are underway to test the biological effects of ΔT (5°C - 10°C) on selected organisms at the three sites. At Kalpakkam, some of the results are proposed to be verified in a small mesocosm study also. A museum of representative forms is also being set up for future reference at the three sites. Details of the preliminary investigations (1.5 year's data) were presented for the three sites by the various PIs at the recently held first National Symposium on Thermal Ecology (NSTE) at Tirunelveli in February, 2002 [8]. It must be emphasised that these initial results need to be validated again and assessed by rigorous statistical analyses before conclusions from this study are drawn.

Towards Evolving a National Perspective on Thermal Ecology

The NSTE symposium provided a forum for the ecologists working under the present CRP to share with the scientific community the unique model pursued by DAE and for interaction of scientists and officials from the statutory bodies. A major goal of the symposium was to sensitise the scientific community and regulatory agencies in this country about the work being undertaken under the DAE-BRNS initiative on Thermal Ecology and to urge other national agencies/industries to undertake similar exercises. The relevance of such efforts is obvious and their implications would hopefully guide the power industry as well as the regulatory agencies in future. It is only through such studies that a national standard for the permissible rise in temperature for discharge of heated effluents into

water bodies under tropical conditions in our country could be arrived at. This might help to drive the power producers to evolve sustainable and “eco-friendly” technologies of power generation. In addition, this will surely help preserve our rich biodiversity. It is hoped that other industries involved in power generation will take a cue from the DAE effort in working out the ecological/environmental costs of their, otherwise beneficial activities.

For studies such as those undertaken in BRNS-CRP on TES to be meaningful, it is important that the work plan is evolved in an interactive mode with the ecologists, power producers, and environmental regulatory agencies. More specifically, the work plan needs to be oriented to address issues and concerns of regulatory agencies. The outcome of this study would evolve a better understanding of the concerns, approaches, priorities and solutions to various aspects of thermal ecology of relevance to sites in our own country for the first time. The study of the impact of heated effluents on tropical aquatic ecosystems would be particularly rewarding as such studies are indeed rare. Since the major advanced countries are located in temperate latitudes, most of the knowledge base in this area has been built up on researches and case studies in temperate waters. Hard data on tropical aquatic ecosystems are lacking. It is desirable, therefore, to obtain such data and update/revise the currently practised legislation regarding discharge of heated effluents. Such researches on the thermal responses of aquatic life-forms, communities and ecosystems should be a high priority now as fear of global and ocean warming and its effect on aquatic ecosystems is becoming more and more closer to reality [9].

References

1. B. Patel, M.C. Balani, S.P. Pandey and S.D. Soman, S.D., International Atomic Energy Agency, Vienna, 1975pp. 17-31.
2. “Environmental effect of cooling systems”, International Atomic Energy Agency, Vienna, 1980.
3. K.V.K. Nair, “Atomic power stations and coastal zone management”, M.S. University, ICASPubl. Proc. Semi. Coast. Mang., 30-37, 1997.
4. T.D. Brock, “Thermopiles : general, molecular and applied microbiology”, John Wiley and Sons, New York, 1986.
5. The Biology of Heat Shock Proteins and Molecular Chaperones” – edited by R. I. Morimoto, A. Tissieres and C. Georgopoulos, Cold Spring Harbor Lab Press, NY, 1994.
6. T.E.L. Langford, “Ecological effects of thermal discharges”, Elsevier Applied Science, UK, pp. 468, 1990.
7. S.K. Apte, “The DAE-BRNS initiative on thermal ecological studies: relevance and implications”, in Thermal Ecology (eds. B. Venkataramani and N. Sukumaran), pp.57-60, BRNS, DAE, Mumbai, 2002.
8. “Thermal Ecology” – compiled by B. Venkataramani and N. Sukumaran, Published by Board of Research in Nuclear Sciences, DAE, Mumbai, 2002.
9. M. Bhaud, J.H. Cha, J.C. Duchene and Nozais, J. Therm. Biol., 20 (1995) 91.