Editorial

George de Hevesy was the first to use radioisotopes as tracers and this heralded the use of radioisotopes as a powerful tool of analysis. In the thirties of the last century, with the construction of accelerators, concept of activation came into existence. Using a radioisotope based neutron source, Hevesy and Levi analysed dysprosium by neutron activation analysis (NAA). Since then, a number of nuclear analytical techniques (NATs) have been developed, demonstrated and are being used. There is neither a unique definition nor a sharp boundary for nuclear analytical techniques. NATs are developed based on the utilization of nuclear properties and are often associated with the phenomena of ionising radiation and isotopes. In NATs elemental concentrations are determined based on measurement of radiations from isotopes. Alpha spectrometry, γ-ray spectrometry, neutron activation analysis, charged particle activation analysis (CPAA), ion beam analysis (IBA), radioimmunoassay and other radiotracer based techniques are some of the popular NATs. Additionally, techniques like PIXE and XRF are considered as NATs as the equipment used in these techniques are same as in some of the NATs. Since isotope properties are used in NATs, it is possible to check the internal consistency, e.g., in NAA, by determining an element through two or more isotopes of the same element. This is feasible because nuclear properties of isotopes like energy and intensity of radiations they emit, half life and formation cross section are unique in most of the cases. Most of the NATs are effective for multi element analysis in a variety of samples and with good detection limits for a number of elements. In the case of NAA, more than 30 elements can be determined from a single experiment. Most of the NATs are contamination free and often non-destructive analysis is feasible.

Selected articles covering NAA, PGNAA, CPAA, IBA and applications of isotopes are included in this issue with an aim of providing the principle of the technique and some applications. I thank all the authors for contributing the articles. It is hoped that these articles would provide the reader with some insight on the various facets of nuclear analytical techniques.

This is the tenth and last issue from the outgoing Executive Committee of IANCAS and I take this opportunity to record my gratitude to all the Guest Editors and authors. My apologies for the delay in bringing out this issue.

CONTENTS

From the Secretary's Desk

Dear Members,

Greetings to the members,

IANCAS has conducted the triennial elections for the executive committee for the term 2003-2005 and my contratulations to all the members of new Executive Committee. This is the last bulletin from the outgoing committee and I take this opportunity to give an account of the progress of our association during the last 3 years. Despite the increase in the life membership fee in the last year, the membership has increased from 872 to 1066 during this three-year term.

Workshops : One of the most popular activities of IANCAS has been conducting BRNS-IANCAS National Workshops on "Radiochemistry and Applications of Radioisotopes". During this term ten Workshops have been organised at the following centers. IANCAS is thankful to coordinators of these Workshops. BRNS has been encouraging and supporting one of the chief 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.

Sr. No.	Place	Period	Coordinators from	
			IANCAS	Host Institutions
1.	M.S. University, Baroda	September 2000	Shri V.V. Ramakrishna Shri D.M. Naronha	Prof. R.S. Somayajulu
2.	BITS, Pilani	October, 2000	Dr. S.K. Samanta Shri A.C. Deb	Prof. S.K. Verma
3.	Ramnarain Ruia College, Mumbai	October, 2000	Dr. A.V.R. Reddy Shri T.P. Chaturvedi	Dr. (Mrs.) K. Raghuraman
4.	K.C. College, Mumbai	December, 2000	Dr. G.A. Rama Rao Shri S.C. Parida	Dr. S. Raghupathy
5.	St. Joseph's College, Tiruchirapalli	April, 2001	Dr. G.K. Gubbi Dr. S. Kannan	Dr. K.V. Raman
6.	IIHR, Bangalore	September, 2001	Dr. K.V. Chetty Shri T.V. Vittal Rao	Dr. S.C. Kotur
7.	Jiwaji University, Gwalior	January, 2002	Dr. V. Natarajan Shri S.C. Parida	Dr. (Mrs.) Radha Tomar
8.	JNV University, Jodhpur	July, 2002	Dr. K.D. Singh Mudher Dr. A.R. Dhobale	Dr. R.P. Tripathi
9.	DDU Univ. of Gorakhpur, Gorakhpur	October, 2002	Dr. N.L. Misra Dr. (Mrs.) Veena Sagar	Prof. N.B. Singh
10.	Goa University, Goa	January, 2003	Dr. G.A. Rama Rao Dr. U.M. Kasar	Prof. K.S. Rane

In continuation to our efforts to popularize the subject of Radiochemistry and Applications of Radioisotopes among the budding students, IANCAS has organized 23 school (one day) and 15 college (two day) lecture-cum demonstration programmes at various centers where IANCAS organized National Workshops in addition to different places in and around Mumbai. IANCAS acknowledges with thanks the efforts rendered by many resource persons from BARC and other units of DAE.

Another popular activityo f IANCAS has been the publication of thematic bulletins. During this term, we have published 10 thematic bulletin in addition to publishing a special bulletin during NUCAR 2003 (details are given in Table 2). I am thankful to all authors, guest editors and editor. Since the response of readers from various areas of specialisation has been so overwhelming, all the thematic bulletins that were published over the years have been compiled into three volumes by Dr. A.V.R. Reddy, Edito. They were released by Chairman, Atomic Energy Commission during the IANCAS function on February 11, 2003, the first day of NUCAR 2003.

TABLE 2. List of Thematic IANCAS Bulletins with Guest Editors and Editors

Sl. No.	Volume	Year	Title	Guest Editor	Editor
1	16(2)	2000	Environmental Quality Monitoring and Assessment	S. Sadasivan	A.V.R. Reddy
2	16(3)	2001	Actinides	V.V. Ramakrishna	A.V.R. Reddy
3	16(4)	2001	Industrial Applications of Radioisotopes	Gursharan Singh	A.V.R. Reddy
4	17(1)	2001	Heavy Water	D.G. Pradhan	A.V.R. Reddy
5	I(1)	2002	Nuclear Reactors	P.N. Prasad	A.V.R. Reddy
6	I(2)	2002	Analytical Spectroscopy	M.D. Sastry	A.V.R. Reddy
7	I(3)	2002	Utilisation of Research Reactors	S.M. Yusuf	A.V.R. Reddy
8	II(1)	2002	Fast Breeder Reactors	P.R.Vasudeva Rao & C.R. Venkata Subramani	A.V.R. Reddy
9	II(2)	2002/03	BRNS interaction with Research Institutes	R.B. Grover	A.V.R. Reddy
10	II(3)	2003	Nuclear Analytical Techniques		A.V.R. Reddy

IANCAS Awards during AGM-2002: The IANCAS-Dr.M.V.Ramaniah Memorial Senior Radiochemist award was bestowed on Dr.S.K.Patil, a former BARC scientist for his life-time contribution in the field of Nuclear and Radiochemistry. The IANCAS-Dr.Tarun Datta Memorial award was presented to Dr. P.N.Pathak, Radiochemistry Division, BARC for his contribution in the field of Nuclear and Radiochemistry relating to studies on the synthesis and evaluation of a large number of alkyl amides for the extraction of uraniuim-233. The IANCAS-Prof. Arnikar Best Thesis award-2001 was presented to Dr.K.Krishnan, Fuel Chemistry Division, BARC for his work on the thermal and structural behaviour of Metal-tellurium-oxygen systems of relevance in nuclear Industry. IANCAS compliments all the awardees. The citations bestowed on them are incl5uded in this issue.

During this period, a southern Chapter of IANCAS has been opened at IGCAR, Kalpakkam with Dr. P.R.Vasudeva Rao as Chairman and C.R. Venkata Subramani as Secretary.

G.A.Rama Rao

Nuclear Analytical Techniques

Editor

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In the radioactive decay characteristic radiations are emitted. Measurement of the energy and intensity of these radiations are useful in the estimation of the radioactive isotopes. With the present day improvements in radiation detectors and associated computer based analysers, it is possible to measure all types of radiations. It is possible to measure individual radioisotopes with high sensitivity which is the most important aspect of any analytical tool. This had led to a rapid growth of the R&D in nuclear analytical techniques.

Neutron Activation Analysis (NAA) is the most popular nuclear analytical technique. In the early development of NAA, ^{266}Ra-Be sources were used and thus it had limited applications. However, in the early 50's when research reactors with neutron fluxes of the order of 10^{12} to 10^{14} were available, NAA got tremendous boost. In the late sixties the availability of semiconductor detectors with resolutions of the order to 2 to 3 keV at 1332 keV enhanced the scope of this technique and about 65 elements of the periodic table with sensitivity in the range of ppt to ppm can be measured. Elements such as those which produce a non-radioactive isotope or a very short lived isotope after neutron capture and those which product only pure β-emitters, can not be analysed with NAA. Such elements can be analysed by measuring prompt gammas which are emitted after the formation of compounds nucleus. This technique is known as prompt gamma neutron activation analysis. This technique requires a neutron beam line facility at the research reactor. Both these techniques have acquired high sensitivities mainly due to the availability of high resolution gamma-ray spectrometry and readers will find the articles on these topics very useful.

In addition to use of neutrons, charge particles are also used in nuclear analytical techniques. With construction of accelerators for charge particle beams like p, d, and heavy ions, ion beam analysis techniques got a boost. The use of charge particle for activation analysis has the advantage that it can be used for those elements where neutron activation is not possible. It can also be used for thin layer activation leading to depth profiling of elements of interest. The other use of light charge particles with energies of the order a few MeV/a is associated with ion beam techniques like RBS, PIX and NRA. Since the charge particle beam can be collimated to very minute size (few microns) this technique is useful for carrying out micro analysis such as distribution of elements in a biological cell. This bulletin contains two good articles on these topics.

Hevesy was the first to use radioactive isotope as a tracer. The tracer application of radioisotope and related techniques such as isotope dilution, radiochemical titration, studies on chemical reaction and synthesis have found a number of applications in chemistry, biology, agriculture, industry and other technology and hence the article on this topic is a good addition. The medical applications of radioisotopes span from diagnosis to therapy. The radio immunoassay, a form of isotope dilution, for assay of trace levels of hormones and viruse,s proteins and other important biological species in fluids has made a great impact on medical science.

The nuclear analytical techniques are useful in R&D in basic science and technology. This field is expanding rapidly and with the advent of better radiation detectors, the scope will further enhance. I thank authorities of IANCAS for asking me to give Focus to this Bulletin which is an opportunity to share my views with the readers of this bulletin.

Nuclear Analytical Techniques

Dr. A.V.R. Reddy *obtained his M.Sc. (Chemistry) in 1974 from Sri Venkateswara University, Tirupati and graduated from BARC Training School in 1967-77. He joined Nuclear Chemistry Section, Radiochemistry Division in 1977 and at present is the Head of the Section. His main areas of research are nuclear fission, nuclear reactions, radiochemical separations and neutron activation analysis. He has more than 150 publications to his credit and co-author of three books. He has worked as a visiting scientist for an year and worked on the extension of periodic table in Institut fur Kernchemie, Mainz, Germany. He was a member of IUPAC's Commission on Radiochemistry and Nuclear Techniques. During 1999-2000, he served as Technical Officer in the Division of Physical and Chemical Sciences, IAEA, Vienna.*

Nuclear analytical techniques (NATs) are developed based on utilization of certain properties of the nucleus and are associated with the phenomena of ionising radiation and isotopes. There is neither a unique definition nor a sharp boundary for nuclear analytical techniques. In NATs elemental concentrations are determined based on measurement of isotopes, in contrast to non-nuclear techniques which utilise the properties of the atom as a whole. Besides nuclear excitations, nuclear reactions and/or radioactive decay, the utilisation of the processes involved in electron inner shell excitations are also regarded as NATs. Additionally techniques like PIXE and XRF are considered as NATs as the equipment used in these techniques are same as in some of the NATs. NATs are divided broadly into two categories namely direct methods and indirect methods, and a select few are illustrated in Fig. 1[1]. Sensitivies that could be achieved by some nuclear analytical techniques like neutron activation analysis are comparable to many non-nuclear techniques like AAS, ICP-AES and ICP-MS and for some elements, sensitivities are superior. Most of the NATs are capable of multi element analysis. In Table 1, capabilities of some NATs with other techniques are compared [2].

Nuclear analytical techniques (NATs) have an advantage over other techniques. Since they use isotope properties, one could check the internal consistency, e.g., in NAA, by determining the same element through two or more isotopes on the same element. This is feasible because nuclear properties of isotopes like half life, energy and intensity of radiations emitted and formation cross section are unique in most of the cases. In tracer experiments, nuclear properties of the radio isotopes are exploited to trace a process or measure the extent of a reaction by using one of the radioisotopes of the element as the tracer since chemical properties of the tracer and tracee are same as they are isotopes of same element. Nuclear radiations like gamma rays, being highly penetrative in the matter, are effectively utilized in diagnostic purposes both in industries as well as in medical sciences. However in the case of some of the ion beam analysis techniques and charged particle activation analysis, essentially information about the surface of the material could be obtained as the penetrating power of the charged particle is very low.

Nuclear Analytical Techniques are quite useful and effective in view of capability of multi element analysis in a variety of samples and with good detection limits for a number of elements. Most of the NATs are contamination free and often non-destructive analysis is feasible. It should be mentioned that the required instrumentation in most of the cases where radio tracers are used is very megre and cost is low. It is also to be noted that most of the facilities like reactor as neutron source and for isotope production, and accelerators as ion beam

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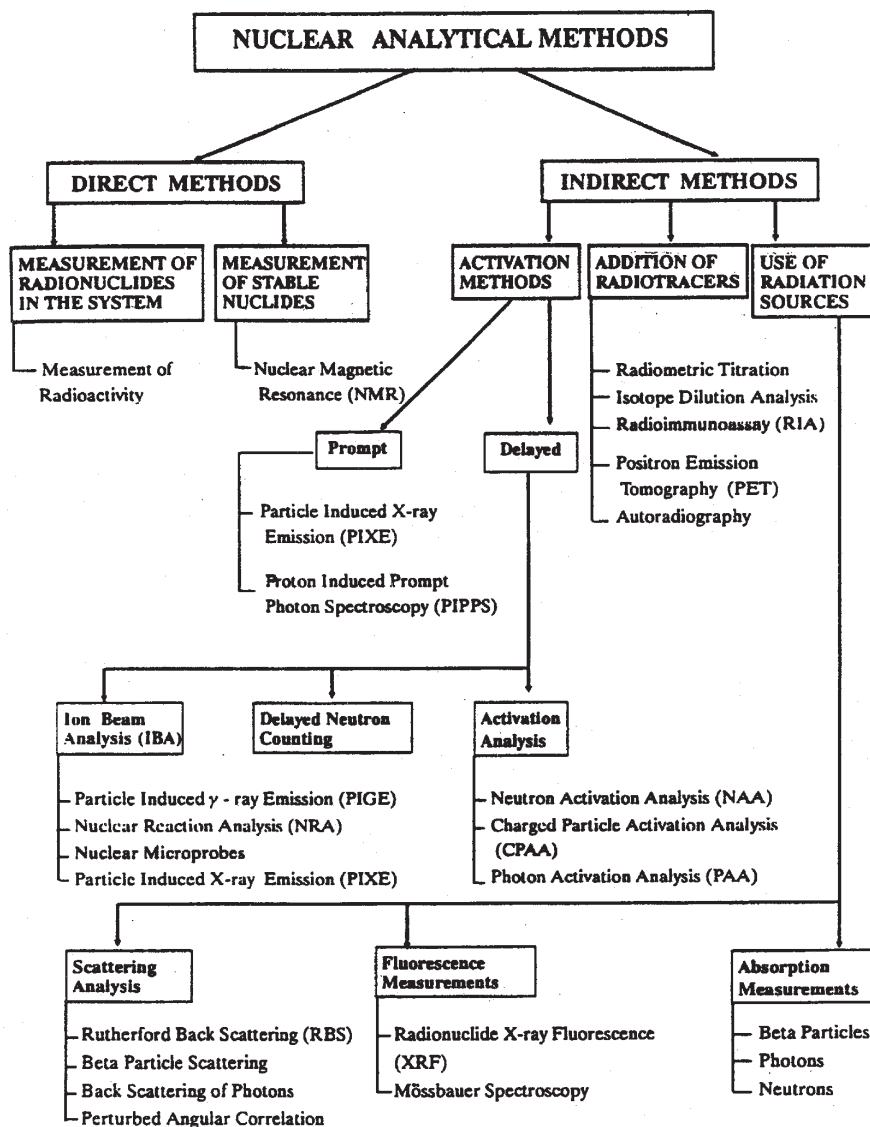E-mail: avreddy@magnum.barc.ernet.in

Fig. 1   Nuclear analytical methods

sources and for isotope production are cost intensive and therefore are located in the major institutes which is a limitation. Additionally, the perception of the educated and not-so-educated about handling of radio isotopes and dealing with ionizing radiations, of late is having a detrimental effect on the expansion and full utilization of NATs.

As it is not possible to include articles on all the nuclear techniques available (Fig. 1), a select few are included in this issue. Neutron activation analysis,

off-line and on line, complement each other. NAA is one of the most used NATs. An article on NAA is included in which various methodologies of NAA and a few applications are described. Prompt gamma neutron activation analysis (PGNAA), an on-line technique where in prompt gamma rays are measured, has an advantage over NAA for determining the light elements. An article describing various aspects of PGNAA is included in this issue. Charged particle activation analysis (CPAA) is another complementary technique to NAA and some

TABLE 1. Comparison of some analytical methods for trace element analysis [Ref. 4]

Method	Accuracy	Sensitivity (S)	Sensitivity (L)	Distribution	Multi-elemental	Sample size	Sample type	Routine	Turn-around time	Accessibility	Costs (S)	Costs(L)
INAA	++	0	0	-	++	mg-kg	S,L	++	-	-	0	0
RNAA	++	++	++	-	0	mg-g	S,L	++	-	-	-	-
XRF	++	-		-	++	mg	S	++	++	++	++	
TXRF	0	0	++	-	++	mg-g	L	++	++	++	0	++
PIXE	-	0		++	++	mg	S	++	-	-	-	
AAS	-	0	++	-		mg-g	L	++	++	++	0	++
ICP-AES	0	0	++	-	++	mg	L	++	++	++	0	++
ICP-MS	0	0	++	-	++	mg-g	L	++	++	0	-	0
ICP-IDMS	++	0	0	-		mg-g	L	0	++	0	-	-

L = Aqueous solution, S = solid, + : good, 0 : average; - : not so good; TXRF : Total reflection x-ray fluorescence; ICP-IDMS : inductively coupled isotope dilution mass spectrometry.

details are provided in an article on CPAA. Ion beam analysis techniques is an emerging technique in materials sciences, though with limitations, and the article on IBA includes the recent experimental findings. Radiotracers play a major role in the applications pertaining to physico chemical sciences, industry, medicine and agriculture. Articles on the use of tracers in separation sciences and agriculture, and an article on radioimmunoassay would provide readers with an insight on the power of tracers for a variety of applications. Gamma ray spectrometry is the most used instrumentation in NATs and details of interaction of gamma radiation with matter and its measurement are described in details in another article.

It is hoped that all these articles will provide the reader with some insight into various facets of nuclear analytical techniques. Facilities for NAA are available at BARC, Mumbai and IGCAR, Kalpakkam; for PGNAA at BARC, Mumbai and for IBA at CCCM, Hyderabad, IOA, Bhubaneswar, IUC, Kolkata and BARC, Mumbai; and for CPAA at VECC, Kolkata. Radioisotopes and the information on the availability of labeled compounds and radioisotopes could be obtained from BRIT, Mumbai by placing purchasing order with BRIT. Two short articles are included on the facilities for NATs at IGCAR, Kalpakkam and VECC, Kolkata.

References

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Neutron Activation Analysis and Applications

Dr. R. Acharya obtained M.Sc. (Chemistry) from Utkal University in 1992. After graduating from BARC Training School in 1993-94, he joined Radiochemistry Division. Since then he is engaged in research and development work on conventional k_0 and prompt gamma-ray neutron activation analysis. The other area of interest is trace element speciation. He obtained his Ph.D. Degree from University of Mumbai in 2000 and has about 70 publications to his credit. He has pursued his postdoctoral studies at Dalhousie University, Canada during 2000-2002.

Dr. A.V.R. Reddy obtained his M.Sc. (Chemistry) in 1974 from Sri Venkateswara University, Tirupati and graduated from BARC Training School in 1967-77. He joined Nuclear Chemistry Section, Radiochemistry Division in 1977 and at present is the Head of the Section. His main areas of research are nuclear fission, nuclear reactions, radiochemical separations and neutron activation analysis. He has more than 150 publications to his credit and co-author of three books. He was a visiting scientist during 1992-93 at Institut fur Kernchemie, Mainz, Germany and worked on the extension of periodic table. He was a member of IUPAC's Commission on Radiochemistry and Nuclear Techniques during 1996-2002. He served as Technical Officerduring 1999-2000 in the Division of Physical and Chemical Sciences, IAEA, Vienna.

Introduction

Neutron activation analysis (NAA) is one of the important nuclear activation analysis techniques [1,2], which is an integral part of nuclear analytical techniques (NATs). The nuclear activation analysis is based on activation of the isotopes of chemical elements and subsequent measurement of induced radioactivity. It provides information on both qualitative and quantitative chemical analysis of samples. The activating source may be a neutron or a charge particle (e.g., α, p) or a photon (e.g., γ-ray) and the radioactive products decay via radiation like α, β, γ and X-ray or delayed neutron. In 1934, I.J. Currie and F. Joliot discovered the nuclear activation by bombarding Al, Mg and B with alpha particles [2]. The neutron induced radioactive product was first reported by Fermi [3]. George de Hevesy and Hilde Levi were first to introduce the NAA technique in 1936. They used neutrons from ^{226}Ra-Be source to activate Dy and Eu in yttrium sample [4,5]. The technique has many advantageous characteristics and is capable of yielding high analytical sensitivity and low detection limits (ppm to ppb). The high sensitivity is essentially due to (1) the irradiation at high neutron flux (10^{11}-10^{15} cm^{-2}.s^{-1}) available from research reactor and (2) counting of sample using high efficiency high-resolution high purity germanium (HPGe) detector. Due to high penetration power of neutrons and gamma rays, matrix effects in the samples of different origins are negligible. During the last 67 years, it has reached to a status of matured reference analytical technique with vast applications in the fields like environment, biology, geology, material sciences, nuclear technology and forensic sciences. This technique is capable of analyzing about 70 elements in the periodic table. The routinely analyzed elements included Na, K, Mg, Ca, V, Al,

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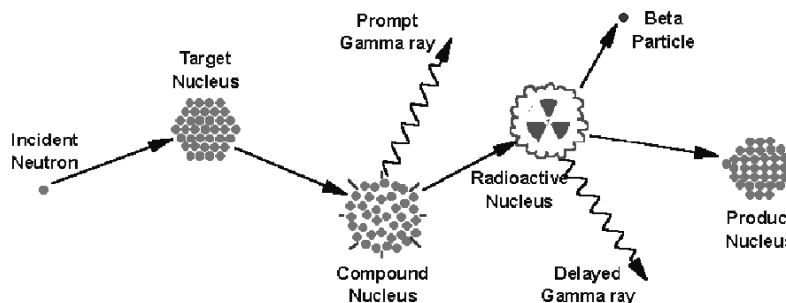
Fig. 1   Interaction of neutron with target nucleus followed by emission of gamma rays

Ti, Mn, Br, Cl, I, In, Sc, Cr, Fe, Co, Ni, Cu, Zn, Cd, Ag, As, Se, Sb, Sn, Hg, Au, Pd, Zr, Hf, U, Th and rare earth elements (REEs). NAA is the most popular and widely used technique for simultaneous multielement analysis at major, minor and trace levels in diverse matrices. The preset article describes the principle, different methodologies and standardization methods giving an overview on the k_0-method, advantages and limitations, areas of applications including some current applications of NAA in our Radiochemistry Division, BARC and future out look.

Principle

Neutron being a non-charged particle interacts with the nuclei of all isotopes forming a radioisotope (activation product) in most of the cases. The NAA technique is based on irradiation of a sample with neutrons, preferably from a nuclear reactor, and subsequent measurement of the induced radioactivity (β,γ) for determination of the concentration of an element [5]. Fig. 1 shows the interaction of neutron with target and subsequent emission of radiation. The decay characteristics permit the unambiguous identification of the radionuclides in the irradiated sample. NAA is carried out by measurement of (i) prompt gamma rays (on line measurement), called as prompt gamma ray NAA (PGNAA) and (ii) delayed gamma rays or other radiations (off-line measurement), called as conventional NAA or simply NAA. PGNAA is mostly carried out using guided neutron beam from reactors. It is complementary to conventional NAA in terms of analyzing some elements including low Z

elements (H, B, C, N, P, Si etc.) [5,6]. The delayed γ-rays are emitted from the radioactive product subsequent to β decay and measurements are off-line.

Radioactivity in NAA

The neutron-induced reactions are energy dependent and (n, γ) are the most prominent reactions [1]. In the nuclear reaction, the rate of formation of the product (daughter) atoms is given by,

$$dN_p/dt = N \sigma \phi - \lambda N_p \qquad (1)$$

where N_p is the number of product atoms formed, N is the number of target atoms of an element in the sample, σ is the (n, γ) capture cross section in barns (cm^2), ϕ is the neutron flux ($cm^{-2}.s^{-1}$) and λ is the decay constant (s^{-1}) of the activation product. A relation for the induced radioactivity ($A = \lambda N_p$) at the end of irradiation can be derived from Eq. 1 as:

$$A = N \sigma \phi (1\text{-}e^{-\lambda t_i}) \qquad (2)$$

where t_i is the duration of irradiation. The activity after a decay period of t_d is given by:

$$A = N \sigma \phi (1\text{-}e^{-\lambda t_i}) e^{-\lambda t_d}$$
$$= (N_A \theta m / M). (\sigma \phi). S. D \qquad (3)$$

where S ($1\text{-}e^{-\lambda t_i}$) is the saturation factor, D ($e^{-\lambda t_d}$) is the decay factor, N_A is the Avogadro number, θ is the abundance of isotope of interest, m is the mass of the element and M is the average atomic mass of the element. The intensity of the characteristic γ-rays of

radioisotopes is measured usig preferably a HPGe based γ-ray spectrometer or less often using NaI(Tl) based spectrometer. The net count rate under a photo peak of is given by,

$$cps = (N_A \theta m / M). (\sigma \phi). S. D. C. \epsilon. \gamma \qquad (4)$$

where C $((1-e^{-\lambda}.CL)/\lambda.LT)$ is the counting factor, which is the correction factor for decay during counting, CL is the clock time, LT is the live time, ε is the absolute full-energy peak detection efficiency and γ is the absolute gamma-ray abundance. When all the parameters in Eq. 4 are known, the quantity of the element (m) can be calculated, in principle, from the measured radioactivity.

Neutron Sources

The neutron sources are primarily of three types; isotopic sources, accelerator based and nuclear reactors [5]. For a limited number of applications isotopic neutron sources based on either the spontaneous fission of ^{252}Cf or nuclear reactions such as (α,n) reactions (like ^{241}Am-Be, ^{226}Ra-Be and ^{239}Pu-Be) or (γ,n) reactions (e.g.^{124}Sb-Be) are used, although they provide a neutron flux which is of several orders of magnitude lower compared to that obtained in nuclear reactors. NAA is also performed using 14 MeV neutrons produced by the (d, t) reaction in neutron generators, or with fast neutrons produced in several nuclear reactions. Nuclear reactors provide the most useful irradiation facilities where high neutron fluxes in the order of 10^{11}-10^{15} cm^{-2}.s^{-1} are available.

Sensitivity and Detection Limit in NAA

The sensitivity (S) of an element in NAA is defined as counts.μg^{-1} for a particular experimental conditions of irradiation (t_i), decay (t_d) and counting (t_c) durations. Depending on the nuclear properties of the isotope of interest, the above parameters (t_i-t_d-t_c) are decided by the analyst. From the Eq. 3, it is clear that the main parameters for sensitivity are σ, φ and ε. Since σ is fixed for an isotope, it is needed to use higher φ and a detector of higher efficiency.

Detection limit in NAA varies from pg to mg depending on the element of interest, gamma ray background, elemental sensitivity, sample matrix and pre or post chemical separations. The detection

limit (L_D) is defined as the three times of the standard deviation of the background counts (C_b) under the photopeak and is calculated using the expression: L_D (counts) = 2.71+3.29x√Cb [7]. The counts are then converted to μg.g^{-1} with the use of S sample mass (g). The typical detection limits using a flux of 10^{13} n.cm^{-2}.s^{-1} are available from the reference [8]. For elements like Eu and Dy, the L_D is about 1 pg whereas for Mn, In and Lu it is 10 pg, for Co, Rh, Br, Au, Re and Sm it is 0.1 ng and for elements like Na, Ga, La, K, Sc, Ni, Zr, Rb, Cd, Zn, and Cr the detection limits are between 10 ng to 1 μg.

Different Methodologies of NAA

The NAA technique can broadly be divided into two categories based on whether analysis of sample is carried out without or with any chemical separation. Depending on the sample type, element and nuclide to be analyzed, different approaches are practised [5,9].

If elements of interest can be determined without any chemical treatment, the process is called instrumental neutron activation analysis (INAA). This approach is more common and has several advantages like non-destructive in nature, multielement capability, minimal sample handling and no reagent blank correction. When the radioisotope of interest is very short-lived (ms to less than a minute) the cycle of to improve the signal to background ratio (S/B) and discriminate the long-lived interfering elements. This approach is called CINAA and it is carried out using automated equipment. short irradiation, quick transfer and short counting of sample. The process is repeated to get accumulated γ-ray spectra for the same sample for an optimum number of cycles (3-4 cycles) depending on the improvements of S/B ratio, counting statistics and also detection limit. When the concentration of element of interest is lower than the detection limit achieved by INAA, then pre or post chemical separations are often employed. In RNAA radioisotopes of interest are separated. When the element of interest is chemically separated prior to irradiation, the procedure is called preconcentration or chemical NAA (PNAA/CNAA). Another pre-irradiation separation approach where speciation/ oxidation state information is obtained in conjunction with NAA is called speciation NAA

(SNAA). For some elements that are poorly determined using conventional NAA or does not have any characteristic gamma lines, derivative NAA (DNAA) is used where the element is chemically exchanged or complexed with an element that is amenable to NAA.

When the element has good nuclear properties and experiences no or minimum interference, the first method of choice is the INAA due to its simplicity. The INAA approach has three different forms depending on the energy of neutron: Thermal INAA (TINAA), Epithermal INAA (EINAA) and Fast INAA (FINAA). The above three INAA methods are named due to activation of isotopes mainly from thermal neutron (most probable energy 0.0253 eV and E_n max up to 0.55 eV), epithermal and resonance neutrons (0.2-500 keV) and fast neutron (>500 keV). In EINAA the total activity due to interfering nuclides such as Na, K, Mn, Cl, Al, Br and La is suppressed. Nuclides of elements, with high resonance integral to thermal neutron capture cross section ratios ($I_0 / \sigma_0 = Q_0$; $Q_0 > 10$), such as Ag, As, Au, Ba, Br, Cd, Cs, Ga, Gd, In, Mo, Ni, Pd, Pt, Rb, Sb, Se, Sm, Sr, Ta, Tb, W, Th and U are analyzed by EINAA. In EINAA the sample is placed inside a cylindrical box of 1-mm thick cadmium (0.55 eV cut-off) or a boron carbide box (cut-off energy 10-280 eV, depending on boron thickness and amount) [5,10,11] and irradiated. The Cd or B absorbs thermal neutrons and filter out higher energy neutrons. The detection limit of these elements is comparable or better than TINAA. However, FINAA is capable of determining many elements including the light elements that are amenable to TINAA or EINAA. The common elements that are determined by FINAA are O, N, F, Mg, Si, P, Fe, Cu, Zn, Zr, Th and U.

Chemical Separations in NAA

RNAA or PNAA methods is attractive for some elements in terms of detection limit, interferences and turn-around time [12]. Additionally, if the sample contains uranium, it undergoes nuclear fission and interferes with elements like La, Ce, Nd, Zr and Mo and thus estimation of these elements would be erroneous. In such situations, it is essential either to preconcentrate and/or to remove elements like U prior to irradiation.

Both separation methods yield better detection limits, however PNAA can give even improved/ lower value than RNAA by using higher mass of the starting material. The PNAA method may suffer from reagent blank. In terms of radiation dose, it is more in the case of RNAA and thus it limits the use of higher mass of the starting material. In the case of SNAA, the species information must be obtained by pre-irradiation separation, since there is a possibility of change of species of elements like Hg and As during irradiation due to rupture of covalent bonds from recoil effect (~10-1000 eV) of capture gamma rays from the compound nucleus [13].

Standardization Methods of NAA

There are three standardization methods of NAA [14,15] as described below.

Absolute Method

The mass of the element (m) can be calculated from measured activity directly using the nuclear and reactor based data. The expression for "m" derived from Eq. (4) is given below.

$$m = \frac{cps}{SDC} \cdot \frac{M}{N_A \cdot \theta \cdot \gamma} \cdot \frac{1}{\sigma\phi} \cdot \frac{1}{\epsilon} \qquad (5)$$

However, this method is not practised for two reasons: (i) it is difficult to evaluate the absolute values of ϕ and σ since both parameter values vary with neutron energy and (ii) uncertainties associated with the absolute values of (n, γ) thermal and epithermal neutron cross sections, γ, θ and M contribute to the final results.

Relative Method

In this method, elemental standard is co-irradiated with the sample and the activities from both sample and standard are measured in identical conditions with respect to the detector. This method is simple to arrive at the results, since it does not need the nuclear and reactor based input parameters. Using the mass of the element in standard ($m_{x, std}$) and activities of standard ($cps_{x, std}$) and sample ($cps_{x, sample}$), the mass of the element in the sample ($m_{x, sample}$) is determined for the same counting time by the following equation:

$$m_{x,\,sample} = m_{x,\,std} \cdot \frac{cps_{x,\,sample}}{cps_{x,\,std}} \cdot \frac{D_{std}}{D_{sample}} \qquad (6)$$

The $m_{x,\,sample}$ (μg) is converted to concentration (e.g., $\mu g.g^{-1}$ or ppm) by dividing with sample mass (g). Though the relative method is simple and precise, prior knowledge of the elements present in the sample is necessary to prepare multielemental standards or certified reference materials (CRMs) of similar matrices.

Single Comparator or k_0-NAA Method

The possibility of using a single element as comparator for multielement NAA (k_0-NAA) [15-18] is attractive The k_0-NAA involves the simultaneous irradiation of a sample and a neutron flux monitor, such as gold, and the use of a composite nuclear constant called k_0. It obviates the preparation of standards for each element and a priori knowledge of constituents of sample is not necessary. For the calculation of elemental concentrations besides net counts under the peak, input parameters [17] such as (i) sub-cadmium to epi-thermal neutron flux ratio (f), (ii) the epi-thermal neutron flux shape factor (α), (iii) the absolute/relative efficiency of the detector (ε) and (iv) the two nuclear constants: k_0 and Q_0 are used. The reactor based parameters (f and α) are dependent on each irradiation facility, so they must be determined for standardization purposes. The factor k_0 is defined as:

$$k_0 = \frac{M^* \theta \, \sigma_0 \gamma}{M \theta^* \sigma_0^* \gamma^*} \qquad (7)$$

where σ_0 is the 2200 $m.s^{-1}$ (n, γ) cross section. The symbol "*" refers to the corresponding parameters of the comparator (e.g., gold). Gold is frequently used comparator in the k_0-method owing to its favorable nuclear properties. However other elements (e.g., Mn, Co, Zr, Zn etc.) can also be used as a single comparator. The k_0-NAA method has been developed using the Hogdahl convention [15] and the expression for concentration of the ith element (C_i in $\mu g.g^{-1}$) is given by [17],

$$k_0 = \frac{\dfrac{N_p / LT}{S.D.C.W}}{\left(\dfrac{N_p / LT}{S.D.C.w}\right)^*} \cdot \frac{1}{k_0} \cdot \frac{f + Q_0(\alpha)^*}{f + Q_0(\alpha)} \cdot \frac{\varepsilon^*}{\varepsilon} \quad (8)$$

where W and w are masses of sample and single comparator respectively. The k_0-factor is taken from the literature by De Corte [18]. The $Q_0(\alpha)$ ($=I_0(\alpha)$ /σ_0) is calculated using following expression

$$Q_0(\alpha) = \frac{Q_0 - 0.429}{\overline{E}_r^{\alpha}} + \frac{0.429}{(2\alpha + 1) \cdot E_{cd}^{\alpha}} \qquad (9)$$

The details of calculations of f, α and elemental concentration in k_0-NAA method can be found in Refs. [19-22]. The Hogdahl convention is not valid for non-1/v nuclides like ^{176}Lu and ^{151}Eu. A convention called modified Westcott-formalism is followed to include these nuclides in k_0-NAA method [23].

The k_0-Based Internal Mono Standard Method

The idea of using an internal mono standard in k_0-NAA is promising in terms of analyzing large and irregular geometry samples [24]. This approach gives relative elemental concentration of element (x) with respect to mono standard (y) as given below,

$$\frac{m^x}{m^y} = \frac{\left((S.D.C.) \cdot (f + Q_0(\alpha))\right)^y}{\left((S.D.C.) \cdot (f + Q_0(\alpha))\right)^x} \cdot \frac{P_A^x}{P_A^y} \cdot \frac{\varepsilon_\gamma^y}{\varepsilon_\gamma^x} \cdot \frac{1}{k_0} \quad (10)$$

where $k_0 = k_{0,Au}(x) / k_{0,Au}(y)$. The relative concentration can be converted to absolute values by using mono standard mass. In special cases where analysis of all major and minor elements is amenable, concentrations can be arrived by material balance.

Advantages and Limitations of NAA

The NAA technique has the advantageous properties [5] like high sensitivity and selectivity, inherent accuracy and precision and low matrix effect in the estimation of many elements. The INAA technique is nondestructive, which helps in minimal sample handling. Both its inherent potentials for accuracy and totally independent principle as a nuclear-based property, which is not the case of many competent techniques, make NAA as an

invaluable reference technique. It has self-validation capability, like a particular element has more than one isotope and one isotope has more than one characteristic gamma line, which forms the basis for an unique ability to verify analytical data.

NAA has some limitations as well [5]. It needs a neutron source like nuclear reactor that is available at a few research centers. Determination of elements forming very short-lived, long-lived or only β^- emission isotopes is difficult by conventional NAA. Determination of elements forming long-lived isotopes is time consuming. NAA is insensitive to the nature of chemical species present unless pre-irradiation separation is carried out. Conventional NAA does not provide sufficient information for certain elements like Si, P, Pb, B, Gd and low Z elements.

Interferences in NAA

The types of interferences in NAA are primary, secondary and second order interference reactions, gamma-ray spectral interference, neutron self-shielding, γ-ray self-attenuation and true and random coincidences during gamma ray measurement [1,5]. If a radionuclide is formed from other than the analyte, then a primary interference reaction occurs as in the case of ^{28}Al, which is produced in the following reactions: ^{27}Al (n,γ) ^{28}Al, ^{28}Si (n, p) ^{28}Al, and ^{31}P (n, α) ^{28}Al. Thus determination of Al in the presence of Si and P is erroneous. However, finding a correction factor or irradiating the sample with and without Cd or B shielding or using a highly thermalized irradiation site can solve these problems. Similarly determination of Mn and Cr in presence of Fe, Na in presence of Al and Mg are other examples. Gamma-ray spectral interferences included 846.8 keV of ^{56}Mn and 844 keV of ^{27}Mg, 279.2 keV of ^{203}Hg and 279.5 kev of ^{76}Se. In such cases other indicator gamma rays are used or one waits for the decay of other nuclide whereever possible.

Experimental Methodology in NAA

In NAA the following steps are involved: (i) sampling, (ii) preparation of sample and standard sample (CRM/ SRM), (iii) preparation of the standard (s) or single comparator, (iv) irradiation of samples and comparator in a reactor, (v) radioactive assay by high-resolution γ-ray spectrometry, (vi) spectral analysis for net peak areas, (vii) evaluation of detection efficiency (for k_0 method), (viii) calculation of elemental concentration, (ix) estimation of uncertainties and (x) interpretation of the results. Details of the various steps can be found in ref. [22].

The k_0-Methodology

The k_0 -NAA method has been standardised and applied to various matrices for multielement analysis by us [22, 25-27]. Standardisation of this method includes; (i) determination of f and α at different irradiation positions of the Apsara, Dhruva and pneumatic carrier facility (PCF) position of Cirus, (ii) dermination of k_0 –factors as part of quality assurance program and (iii) validation of the method, evaluating the precision and accuracy by analysing CRM/SRM of different origin. In view of the utilisation of various irradiation positions in the reactors, values of "f" and "α" were determined by bare and/or cadmium ration methods using monitors like ^{197}Au, ^{94}Zr and ^{96}Zr. The f and α values were obtained by cadmium ratio method and they are 52.2±2.7 and -0.016±0.004 [26] for E8 position of Apsara. A library of k_0 -factors for 111 radionuclides spanning from fluorine to uranium was compiled taking gold as the comparator [25] out of which k_0 -factors for about 38 radionuclides were experimentally measured [22]. A variety of the standard reference materials like AGV-1 and W-1, NOD-A-1, SOIL-7 and SRM-1571 are routinely analysed using the k_0 -standardised NAA to validate the method in terms of precision and accuracy. The % deviation of measured values from certified ones are plotted I Fig. 2. The % deviations for many elements were within ±10% [27].

Applications of NAA

NAA has found extensive applications in many science and technology fields for macro, micro and trace element analysis in the samples corresponding to the following fields [28]: archaeology, biomedicine, animal and human tissues, environmental science and related fields, forensics, geology and geochemistry, industrial products, nutrition, quality assurance of analysis and
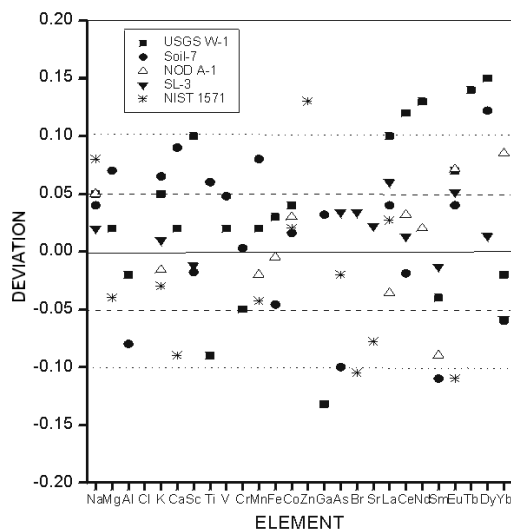
Fig. 2 *Comparison of measured and certified elemental concentrations in five reference materials*

certifications reference materials. Two such applications are described here.

Certification of Reference Materials

The NAA methods have played an important role in the certification of inorganic constituents in many environmental certified/standard reference materials (CRMs/SRMs) [28]. Since the concentration of an element in CRM/SRM certified by agencies like NIST, IAEA, IRMM and USGS is usually determined by two or three independent analytical methods, the use of INAA as one method eliminates the possibility of common error sources resulting from sample dissolution. Other advantages include: its property in its radiochemical mode of allowing trace element radiochemistry to be performed under controlled conditions by carrier additions, and the ease of obtaining the chemical yield by the carrier recovery or radiotracer method. More over, the method is theoretically very simple and the sources of uncertainty can be modeled and well estimated as per the international organization for standardization (ISO) guidelines.

The estimation of combined uncertainty is an independent exercise and it is different than the calculation of standard deviation from the mean value of replicate measurements [29]. The different uncertainty components were divided into three steps: pre-irradiation step, irradiation step and gamma ray spectrometry measurement step. An additional step is considered if chemical separation step is done. The sources of uncertainty are identified and then each uncertainty component (u_i) is converted to a standard deviation. The combined uncertainty (u_c) is calculated using error propagation formula. Finally the expanded uncertainty (EU) is calculated using coverage factor of 2 at 95.5% confidence level (CL).

Forensic Applications

INAA/RNAA methods are frequently used for analysis of forensic samples like gun shot residues, glass, hair, ornamental gold, cannabis and paper [30]. Some of the marker elements such as Ba, Sb, Cu, Sb, Ag, Fe, Br, Zn and K are analyzed depending on the sample type.

Our Work on NAA

The k_0-method was developed by us at our facility and has been applied for the multielement profiles and derived studies in samples like ruby [26], emerald and associated rocks [31], manganese encrustation [32], sediments from Nainital Lake [33], cereals and pulses [34] and medicinal leaves [35]. Additionally, both Radiochemical NAA (RNAA) and Chemical NAA (CNAA) methods were adopted [36] for the determination of trace elements in standards and samples of leaf matrix after sequential removal of Br by oxidation and Na and K (partly) by Hydrated Antimony Pentoxide (HAP). In an other case a pre-concentration NAA procedure was standardized using anion exchanger, Dowex-1X8 in chloride form for the determination of palladium in matrices containing Fe, Cu and U. Under the ideal interference free conditions, an absolute detection limit of 0.12 ng for palladium was achieved [37]. A DNAA method has been standardized for the determination of phosphorous in water and biological matrices [38].

Determination of Total Arsenic in Drinking Water and its Speciation

Arsenic has received increased attention in recent years because of its toxic and carcinogenic properties. The maximum permissible limit in

Table 1 - Concentration values ($\mu g.L^{-1}$) of arsenic of some drinking water samples from West Bengal.

Sl. No.	Location (district)	Water source	Concen- tration
1	North 24-Praganas	Tube well	20±3
2	North 24-Praganas	Tube well	47±4
3	North 24-Praganas	Tap water	95±10
4	North 24-Praganas	Tube well	210±12
5	Nadia	Tube well	122±8
6	Murshidabad	Tube well	524±20
7	South 24-Praganas	Tube well	644±26

Table 2 - Elemental concentrations ($mg.kg^{-1}$ unless % is indicated) of zircaloy-2 plate.

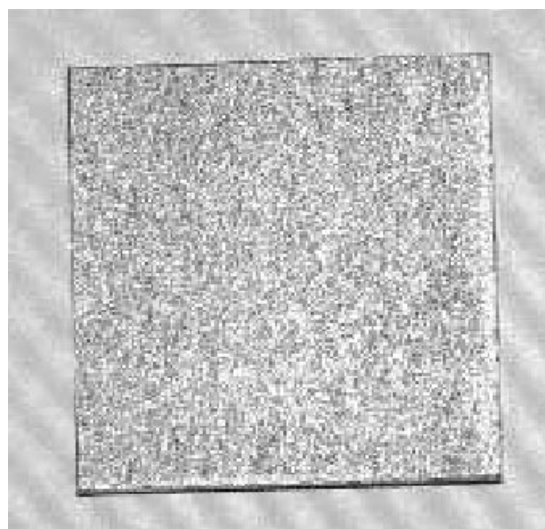| Element	Zircaloy-2	ASTM Specification
As	4.49±0.21	NA
Cr%	0.099±0.007	0.05-0.15
Fe%	0.188±0.007	0.07-0.2
Hf	23.9±1.0	NA
In	0.35±0.01	NA
Mn	19.5±0.2	NA
Ni%	0.092±0.001	0.03-0.08
Sn%	1.50±0.07	1.2-1.7
Zr%	98±1	Balance

drinking water set by World Health Organization (WHO) is 10 $\mu g.L^{-1}$. In view of this, INAA method was applied for the determination of total arsenic in drinking water samples from different districts of West Bengal. Table 1 shows the arsenic concentrations of a few water samples which vary from 20-644 $\mu g.L^{-1}$. Additionally, two ion exchange separation methods have been standardized for the speciation of As(III) and As(V) in aqueous samples. Synthetic mixtures of As(III) and As(V) in aqueous systems were separated by ion exchange chromatography and the concentrations of the separated fractions were determined by INAA [39].

Analysis of Large and Non-Standard Shape Samples

A k_0-based internal mono standard method has been standardized to analyze irregular geometry and large size samples. Samples are irradiated in highly thermalized positions of a reactor to circumvent neutron flux perturbations and an in-situ relative detection efficiency was to circumvent in the γ-ray self-attenuation . The method was standardized with added impurities in 0.5 kg silica [40] and 0.5 L water. The method has been successfully applied to a non-standard geometry sample of a zircaloy-2 plate of 67 g (Fig. 3). The sample was irradiated in thermal column at Apsara reactor and assayed by gamma ray spectrometry. The in-situ detection efficiency was

Fig. 3   The zircaloy-2 plate (67 g)

determined using gamma lines of ^{95,97}Zr, ^{56}Mn and ^{116m}In (Fig. 4). The complete compositional analysis was done via mass balance.

Future Perspective of NAA

The future position of NAA among alternative trace element analysis techniques will depend strongly on further development and exploitation of the advantages and reduction of the drawbacks. Applications of NAA should be selective, exploiting the specific advantages of the technique and
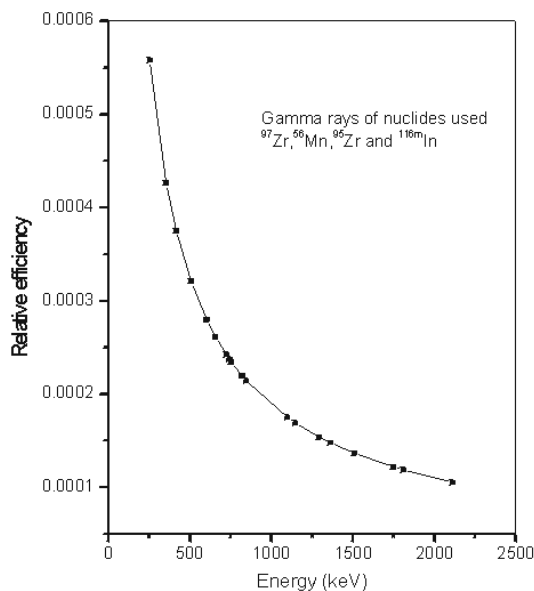
Fig. 4 *In-situ relative efficiency of zircaloy-2 plate*

avoiding application where NAA is clearly not the method of choice. Applications where NAA can be used advantageously include the use when high accuracy is required (i.e., as a reference method), for the analysis of large and non-standard size and shape, and for samples that have to be preserved after irradiation and analysis. Use of clean laboratories (Class 100 or 10) and quality chemicals to avoid contamination for pre-irradiation separations in PNAA would help in enhancing sensitivity. Judicious use of relative and k_0 standardizations of NAA may be of considerable help in analyzing all the elements in a sample. PGNAA method can be advantageously used for determination of low Z (H, Li, B, C, N, P, S, Si) and other elements (Gd, Pb, Hg, Cd, etc.). The selection of a method from different methodologies in conjunction with special counting techniques, such as anticoincidence gamma ray spectrometry using Compton suppressed system is considered useful.

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Prompt Gamma Neutron Activation Analysis

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Introduction

Prompt Gamma Neutron Activation Analysis (PGNAA) is a technique for the analysis of elements present in solid, liquid and gaseous samples by measuring the capture gamma rays emitted from a sample during neutron irradiation. The reaction is written as T(n,γ)P where T is the target nucleus and P stands for the product. The reaction is called radiative capture of neutrons. The technique is complementary to conventional neutron activation analysis (NAA) as it can be used in a number of cases where NAA fails. Though the technique was first used in sixties [1], the advantage of the technique was first highlighted by Lindstrom and Anderson [2]. PGNAA is increasingly being used as a rapid, instrumental, nondestructive, and multielement analysis technique. A monograph and several excellent reviews on this topic have appeared recently [3-6]. In this article, an attempt is made to bring out the essential aspects of the technique,

experimental arrangement and instrumentation involved, and areas of application.

Fundamentals of PGNAA

Capture gamma rays are also called prompt gamma rays since they are emitted within about 10^{-12} s of capture of neutron by an atomic nucleus. So neutron irradiation and gamma ray counting of the sample is done simultaneously in PGNAA. It is therefore an on line technique and preferably requires a "Neutron Beam" facility for irradiation of targets. On the average 3-4 γ rays are emitted per neutron capture and they carry off about 7-10 MeV excitation energy, which is the average binding energy of a neutron in a nucleus. The prompt gamma rays can therefore have energies in the range of a few keV to about 10 MeV. This is to be distinguished from NAA where the gamma rays emitted following beta decay of an activated sample are counted and their energies are up to about 3 MeV. The prompt gamma rays are characteristic of the isotopes of

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elements and practically isotopes of all elements absorb neutron and emit prompt gamma rays. Hence elements in the entire periodic table can, in principle, be measured using prompt gamma rays. However, so far the largest number of publications on PGNAA appeared on the determination of low Z elements (H,B,C,N,Si,P,S,Cl) and trace elements with large neutron absorption cross section (Hg, Cd, Sm, Gd). The advantages of the technique can be summarized as: (1) ability to determine light elements (H,B,N,C,P,S,Si) and hence analysis of biological samples possible, (2) ability to determine toxic elements (Cd, Hg) with high sensitivity and hence can be used for analysis of environmental samples, (3) nondestructive multielemental bulk analysis is possible which offers the flexibility of sample size and shape and can be particularly suitable for archeological, geo- and cosmo- chemical samples (4) isotopic analysis is possible (S,Si,Ni) in some cases and (5) because of higher γ ray energy, there is minimum attenuation in the sample, and hence larger sample size can be used for the analysis. The major disadvantages of the method are: (1) the prompt gamma ray spectra are very complex, often containing several hundred peaks and invariably has to be analyzed by peak fitting software, (2) a separate neutron beam facility is required, (3) existing prompt gamma ray data are inadequate and (4) sensitivities for most of the elements are lower than conventional NAA.

Neutron Beam Facilities

In general neutron beam lines used for prompt gamma experiments can be broadly classified as:

Guided Beam

Here neutron beam is transported from reactor core to experimental site through a beam tube. This offers the following advantages, (1) low stray neutron and gamma ray background, (2) both thermal and cold neutron beam can be used and (3) minimal interference from fast neutrons due to resonance. Cold neutron beams offer higher sensitivity due to enhanced absorption cross section arising from 1/v law, and higher beam intensity.

Diffracted Beam

Neutron beam coming out of reactor core is reflected by a suitable crystal and taken to the experimental site. In this case also high gamma ray background of the radial neutron beam is avoided. Here beam is composed of neutrons having selective wavelengths.

Spallation Neutron

Neutrons emitted from a spallation reaction in a cyclotron are thermalised and used as beam. The characteristic of such a beam is that there is no gamma ray background associated with a reactor, in addition to obtaining higher neutron beam intensity. PGNAA is also carried out using portable neutron sources (^{252}Cf, neutron generator) for field work. This will not be included for discussion in this article.

Shielding

Since stray neutron and gamma ray background are usually very high around a neutron beam line, detector shielding is an important aspect of a PGNAA set up. Gamma ray background is reduced using a thick lead shield while neutron absorbers like B and Cd can be used for neutron shielding. However, B and Cd produce 478 keV and 559 keV (and higher energy) γ rays respectively on neutron absorption which contribute to the background. Neutron reacts with the detector cover cap and Ge to produce ambient gamma ray background. Hence enriched ^{6}Li in the form of LiF ceramic tile or sheet is commonly used as cover cap of the detector to prevent the neutron from entering the detector. ^{6}Li (n,α)^{3}T reaction does not produce any γ ray. Reference 3 gives a good account of the experimental set up, instrumentation and shielding aspects of PGNAA. A schematic diagram of the experimental arrangement is given in Fig. 1.

Target Preparation and Irradiation

Normally targets in the range of 0 .1- 1 g in powder, pellet or disc form are used for irradiation. Size of the target should be less than the neutron beam size. If comparison with a standard is done, then errors due to matrix effect (neutron self shielding, neutron scattering, gamma ray attenuation, and change in detector efficiency due to
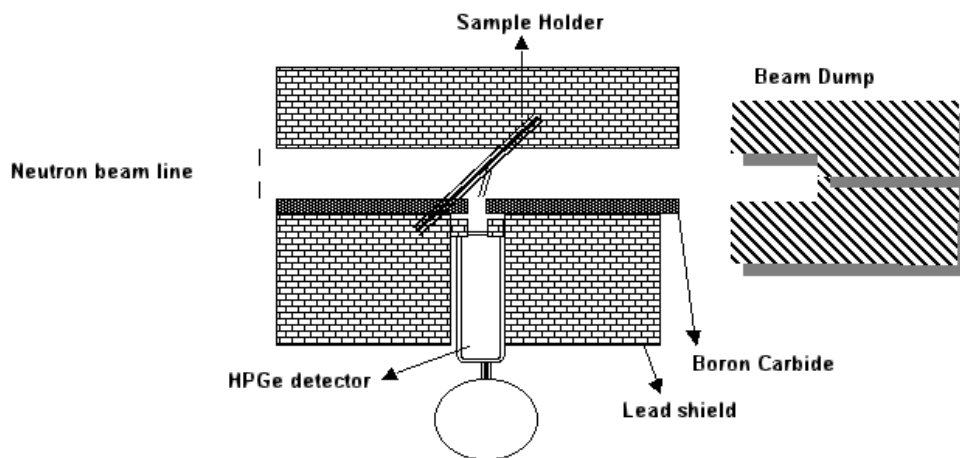
Sample Holder

Beam Dump

Neutron beam line

Boron Carbide

HPGe detector

Lead shield

Fig. 1   Schematic representation of the PGNAA set up

sample geometry) can be minimized by matching sample geometry and matrix as closely as possible to that of the standard.

For irradiation, samples are usually wrapped or sealed into Teflon bags and suspended in the path of the neutron beam using Teflon string. Teflon produces minimum background since both fluorine and carbon have low neutron absorption cross sections of the order of millibarn (mb). If fluorine is to be measured, plastic packets can be used. Since scattering cross section of hydrogen is very high (80 barn), use of hydrogenous material for target packing is normally avoided. Unless analysis of trace level of nitrogen or hydrogen is required, irradiation is carried out in air.

Instrumentation

Instrumentation needed for PGNAA and INAA are same viz. a high resolution and high efficiency γ ray spectrometer system. A large volume HPGe detector is required since measurement of high energy γ rays is involved. In order to reduce the Compton background in the spectra, the HPGe detector is often used with an anti Compton annular BGO (Bismuth Germinate) shield which surrounds the HPGe detector. In this case, a coincidence measurement is needed and the electronics set up becomes slightly involved. Since a Compton scattered gamma ray from HPGe detector is intercepted by the anti Compton shield, the signal

from HPGe detector is rejected if it is associated with a signal from the shield. Thus the Compton background can appreciably be reduced, which in turn improves the detection limit of measurement. Since pair production becomes the primary mode of interaction for high energy γ rays (say 5 MeV and above) in the detector material, higher energy portion of the prompt gamma ray spectrum is complicated by the presence of single and double escape peaks in addition to the full energy peak. Thus every γ ray produces three peaks. Figure 2 shows the higher energy part of ^{60}Co spectrum. The single and double escape peaks are marked in the spectra. In order to reduce the complexity, the anti Compton shield is also used in pair spectrometer mode . In this case , the coincidence signal from the two segmented halves of the shield in association with the HPGe detector signal is registered as a valid event. Thus the higher energy portion of the spectra becomes free from the photo peak and single escape peak, thereby making the spectra simpler. However, the electronic set up becomes more involved. In practice, data acquisition is simultaneously carried out in singles, anti-Compton and pair mode and sorted out during the data analysis time. Data acquisition is done in a pulse height analyzer (PHA) with 8k or 16k memory.

Data Analysis

Prompt gamma ray spectrum from a sample of simple matrix can be quite complex. Figure 3 shows
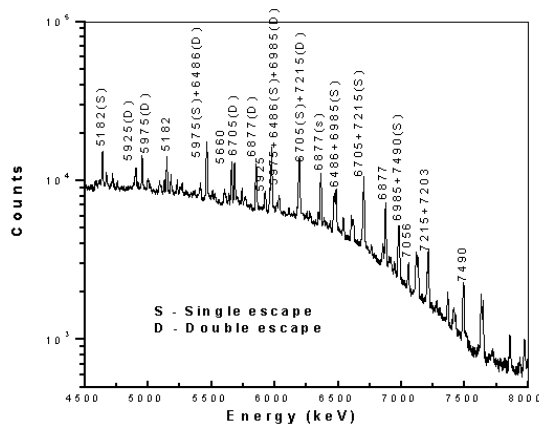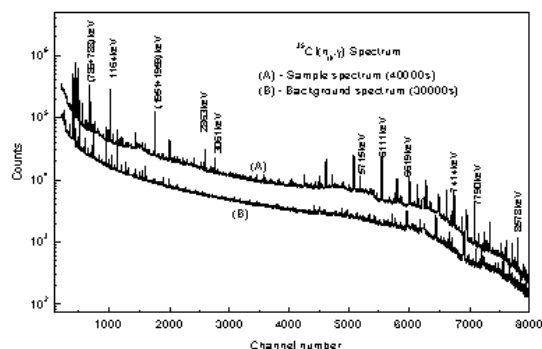
Fig. 2   *Higher energy spectrum of ^{60}Co*

Fig. 3   *Prompt gamma-ray spectrum of NH$_4$Cl with background*

a typical prompt gamma spectrum of NH$_4$Cl acquired using an HPGe detector in the guided beam facility of DHRUVA reactor. Important peaks for ^{35}Cl(n,γ) reaction are marked in the spectrum. For our work, we used the PHAST software developed at the Electronics Division, BARC for spectrum analysis. In PGNAA, no saturation and decay corrections are involved and the observed peak areas can be directly used for the analysis of elements. So far there is only one tabulation of neutron capture prompt gamma ray data [7]. However, new and refined tabulation based on isotopes is under preparation which would improve the results of analysis using prompt gamma ray measurement.

Methodology

The count rate R (cps) due to ith isotope of an element present in the sample is given as:

$$R(CPS) = W\theta_i N_0 \sigma_i \phi a_i \varepsilon_i / M \tag{1}$$

Where W is the weight of the element in the sample and M is its atomic weight. θ_i, σ_i, a_i are the isotopic abundance, cross section and gamma ray abundance of the ith isotope of the element of interest. ε_i is efficiency of detection of the gamma ray of interest. N_0 and ϕ are the Avogadro number and flux of the neutron beam respectively. For this equation to be valid, sample size has to be less than the beam size. As evident from the above equation, the detection sensitivity of an element is given by the product $(\theta_i \sigma_i \phi a_i \varepsilon_i)$ and higher value of any one of the parameters enhances the sensitivity of detection.

Four different methods can be used to carry out elemental analysis using PGNAA. They are:

1.   Absolute Method

In this method, the measured count rate due to an isotope is directly converted to weight (W) of the corresponding element in the sample using the equation:

$$W(g) = R(cps) M/\theta_i N_0 \sigma_i \phi a_i \varepsilon_I \tag{2}$$

The method requires the knowledge of neutron flux, literature value of σ_i, a_i and experimental determination of ε_i. This method is not used in practice.

2.   Relative Method

In this method, weight of an element (W_u) in a given matrix is determined with reference to a standard (W_s) using the relation:

$$W_u = W_s (CPS)_u / (CPS)_s \tag{3}$$

Advantage of this method is that flux monitor and nuclear constants are not needed. The disadvantage being, sample and standard cannot be irradiated together so the matrix effect (self absorption and scattering) and geometrical difference between sample and standard affect the accuracy. This method is commonly employed for the analysis.

3. Single-comparator (Mono-standard) Method

One can obviate the need of multi elemental standard by the use of a mono-standard method, also known as k_0 standardisation method. In this approach, the sample is co-irradiated with a suitable comparator element like chlorine (salt form) and titanium. In order to use this method for elemental analysis a k_0 factor, which is a measure of elemental sensitivity ratio of the isotope of element of interest (x) to the comparator (c), corrected for the effeciencies, has to be determined in advance. The factor is given as:

$$k_{0,c}(x) = (A_{sp}/\varepsilon)_x/(A_{sp}/\varepsilon)_c = M_c(\theta_i \sigma a)_x / M_x(\theta_i \sigma a)_c \quad (4)$$

Here (A_{sp}/ε) refers to specific count rate corrected for the efficiency. The first part is experimentally measured and the second part can be evaluated using the nuclear data from standard compilations. Details of this method are given in ref. [4]. The k_0-factors or relative sensitivities depend on cross section ratios which depend in turn on the shape of neutron spectrum. Thus it is recommended that to the factors are determined for a given facility. Once the $k_{0,c(x)}$ factors are determined with respect to a comparator, elemental concentration (C_x, µg/g) can be found out using the formula:

$$Cx = \frac{A_{p,x}}{A_{sp,c}} \frac{1}{k_{0,c(x)}} \frac{\varepsilon_c}{\varepsilon_x}$$

where $A_{sp,x}$, $A_{sp,c}$, and ε stand for specific count rate per gram sample, specific count rate per µg of the comparator, and efficiency of the detector respectively. Here x and c stand for unknown element and comparator respectively. Tabulation of $k_{0,c(x)}$ factors are now available for important gamma lines for most of the isotopes of elements spanning entire periodic table [9] and general consensus is that, for those nuclei which follow 1/v law for neutron absorption, these factors do not depend on the neutron spectrum provided it is thermalised as in the case of guided cold or thermal neutron beam line. However whenever the scattering and neutron absorption property of the standard and comparators are different, the factors can deviate from quoted values. We determined several k_0 factors using the guided beam line of DHRUVA reactor for different elements [10] with respect to 1951 keV gamma line of ^{36}Cl and Table 1 gives the values along with the literature values. Except for the non 1/v nuclei like Cd, Gd and Sm, the overall agreement between measurements of different laboratories indicate the stabilities of the k_0 factors. Most elements form stoichiometric compounds with chlorine and prompt gamma rays of ^{36}Cl spans over 500-8500 keV, hence it is chosen as a comparator. The values are determined mostly using chloride compounds of the elements. The single comparator method has been popular for the elemental analysis of samples by PGNAA.

4. Internal Monostandard (weight ratio) Method

In this case, weight ratio of the elements(x) with respect to a particular element(y) in the sample is determined using the k_0 factors.

$$\frac{W_x}{W_y} = \frac{\left[A_x / \varepsilon_x k_{0,c}(x)\right]}{\left[A_c / \varepsilon_c k_{0,c}(y)\right]}$$

A refers to observed peak areas. If concentration of the comparator element is determined by some other method or already known then concentration of other elements in the matrix can be obtained. In favourable cases when the ratios are obtained for all the major and minor elements of the matrix by PGNAA, then absolute concentration can be found out by material balance equation. This method has the advantage that the matrix effect can be minimized. This method is truly nondestructive, and can be adopted for analysis of samples of irregular size and shape.

Application

PGNAA using thermal and cold neutron beam has been used for multielement analysis of a wide variety of samples. As stated earlier, most of the applications have been for determination of low -Z elements which cannot be determined by NAA. Figure 4 shows the detection limit for some elements as determined by Yonezawa [11] for their system at JAERI. Detection limits for H, B, Cl, Co, Cd, Sm, Gd, and Hg are at ppm or sub ppm level. For other elements it is mostly in the range of 100 µg/g level or above. This limit will obviously vary depending upon the intensity of the neutron beam, ambient back

Table 1. Measured and reported prompt k_0 factors with respect to 1951 keV gamma lines of ^{36}Cl

Element	Sample compound	Capturing Isotope	Gamma-ray used (keV)	$k_{0, Cl}$ Measured	$k_{0, Cl}$ Reported	
					Ref. 9[#]	Ref. 8
H	NH_4Cl	^1H	2223	1.86±0.07	1.80±0.016	1.80± 0.061
B	H_3BO_3+ NH_4Cl	^{10}B	478	312± 22	360±3.4	367± 13
K	KCl	^{39}K	770	0.116± 0.004	0.127±0.002	0.127±0.0043
Ca	$CaCl_2.2H_2O$	^{40}Ca	1942	0.045±0.002	0.0464± 0.0014	0.0469± 0.0019
Cl	NH_4Cl	^{35}Cl	786+788	1.30 + 0.026	NR	1.33 +0.045
Co	$CoCl_2.2H_2O$	^{59}Co	230	0.58± 0.04	0.66±0.01	NR
			277	0.55± 0.04	NR	0.619± 0.021
			555	0.456± 0.026	0.275[*] ± 0.004	0.516± 0.018
			1516	0.186± 0.006	NR	NR
			1831	0.191± 0.010	NR	NR
			6485	0.185± 0.015	NR	NR
			7215	0.156± 0.006	NR	NR
Ti	Ti+ NH_4Cl	^{48}Ti	342	0.187± 0.006	NR	NR
			1381	0.604± 0.013	NR	NR
			1585	0.056± 0.003	NR	NR
Cu	Cu+ NH_4Cl	^{63}Cu	278	0.068±0.004	0.083[*]± 0.002	0.0766± 0.0027
			385	0.0187± 0.0010	NR	0.0174± 0.00070
			7306	0.0261± 0.0014	NR	NR
Cd	$CdCl_2.2.5H_2O$	^{113}Cd	558	41±2	90.5[*] ± 1.7	81[*]± 2.3
Ba	$BaCl_2.2H_2O$	^{138}Ba	627	0.0106± 0.0003	0.01164± 0.00027	0.0111± 0.00040
		^{135}Ba	819	0.012± 0.002	0.00842± 0.00019	NR
		^{137}Ba	1435	0.011± 0.001	0.01224± 0.00033	NR
Hg	$HgCl_2$+ NH_4Cl	^{199}Hg	368	5.8± 0.3	1.44[*] ±0.059	7.1[*] ± 0.26
			1693	1.37± 0.08	NR	NR
Cr	$CrCl_3.6H_2O$	^{50}Cr	749	0.065± 0.008	0.0598± 0.0013	NR
		^{53}Cr	834	0.138± 0.008	0.0145± 0.0038	0.142± 0.0049
		^{52}Cr	7938	0.0477± 0.0030	0.0445± 0.0012	NR
Gd	Gd_2O_3+ NH_4Cl	^{157}Gd	1186.7	111±4	109±6.6	NR

NR - not reported. Errors given are 1σ uncertainties on multiple measurements
[#] values converted from $k_{0, H}$ from ref 9.
[*] Indicates the cases where difference of k_0 values expressed as absolute value of z-score exceeds 3 with respect to present work

ground condition, and detection efficiency of gamma rays. Rossbach [12] used this method to characterize biological samples for bulk elements H, C, N, S, Cl, K, and trace elements like B,F, P,V, Cd, Sm, Cd. Extensive work on determination of hydrogen in a variety of matrices has been done at NIST [13]. Boron is one of the most sensitive elements in PGNAA and it has been widely used to determine boron in rock samples [14], high purity Si wafer [15] and human tissue during boron neutron

capture therapy (BNCT) [16]. PGNAA has also been used for isotopic analysis of S, Si and Ni [17]. Since it is possible to do multielemental analysis nondestructively with samples of different size and shape, PGNAA is finding wide application for analysis of archeological, geo- and cosmo- chemical and other bulky samples [18-20].

Experiments on PGNAA were carried out using the guided as well as diffracted beam facility at DHRUVA reactor. Determination of efficiency of
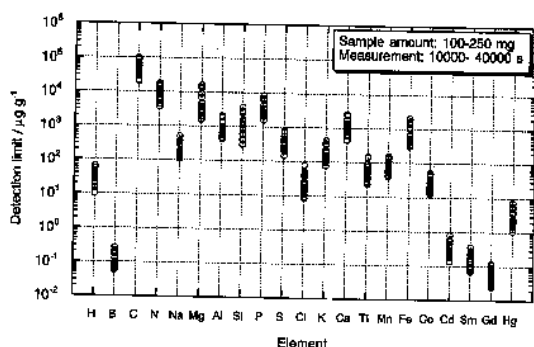
Fig. 4   Detection limit of element in various materials [11] .

Fig. 5   Absolute efficiency curve (PGNAA system, Dhruva)

detection of gamma rays is essential for any k_0 based PGNAA work and has been determined for our work using the prompt gamma rays of chlorine (^{36}Cl), titanium(^{49}Ti) and the delayed gamma rays of ^{152}Eu. Figure 5 shows the efficiency curve generated using a fifth order polynomial fit [21].Using the diffracted beam facility of Dhruva reactor, analysis of some standard alloy samples were performed by the internal mono standard method. The details of the procedure for in situ efficiency generation, required for the analysis, is given in ref. [22].

Conclusions

PGNAA is a non destructive multielement analysis method. It is a complementary technique to conventional NAA. The method is especially suitable for the determination light elements like H,B,N,C,P,S and Si and elements of high neutron absorption cross sections like Hg, Cd, Sm and Gd. Use of k_0 based PGNAA can be advantageously used for the analysis of wide variety of samples. It offers the possibility of analysis of samples of non standard size and shape.

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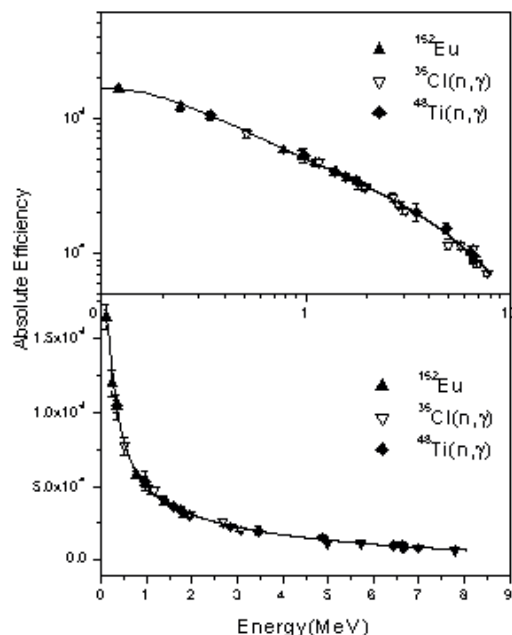
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Charged Particle Activation Analysis and its Applications

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Introduction

Charged particle activation analysis (CPAA) is based on the charged particle induced nuclear reactions using high energy particles from the accelerators. CPAA is one of the most sensitive and highly efficient nuclear analytical techniques [1-3] for the determination of elemental concentration at trace and ultra trace levels in a sample. CPAA is a complimentary technique to neutron activation analysis (NAA) to make the activation analysis a versatile analytical technique for the determination of almost all the elements in the periodic table. In the last three decades, CPAA has been applied for the determination of trace elements in the research and development works in the basic sciences as well as in applied areas. Its application includes the characterisation of high purity materials, semiconductors, optoelectronic materials, petroleum oils, geological materials, etc. CPAA has been developed and standardised using available charged particles (proton and α-particles) from Variable Energy Cyclotron machine at Kolkata. CPAA has been applied for the determination of trace elements in high purity metals, semiconductors, geological materials and petroleum oils.

General features of CPAA

Characteristics of CPAA

The most commonly used charged particles are: triton – 3 to 4 MeV; proton, deuteron and ^{3}He – 5 to 20 MeV; α-particles – 20 to 45 MeV. Among these triton and ^{3}He are best suitable from the consideration of sensitivity and interference. However, both triton and ^{3}He are not easily available from the accelerators. Proton, deuteron and α-particles are also suitable for the elemental characterisation at ppm to ppb levels and widely available for CPAA applications. One interesting feature of CPAA, contrary to NAA, is that numerous reactions are possible from a target atom as shown in Fig. 1. The chances of getting a suitable isotope remain more for the determination of the target atom in CPAA. The sensitivity of CPAA is very high largely because of availability of high particle flux, 10^{12} to 10^{14} particles per sec and high cross sections (the hundreds of millibarns). The detection limits of the elements in the periodic table for the CPAA applications are shown in Fig. 2 and these are obtained based on the best reaction and irradiation conditions. The most striking feature is that the detection sensitivities of low Z elements, boron, carbon, nitrogen and oxygen, are in the order of sub ppb levels.

Excitation Functions and Activation Curves

The study of excitation functions and activation curves [4] is a prerequisite in CPAA application. As the cross section of the reaction varies with the energy of the charged particles, i.e. excitation functions, yield of the activation products is dependent on energy. The selection of energy of the particles comes from the study of excitation

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Fig. 1   Produts of charged particle reactions induced on a target nucleus (black field)

functions or activation curves. Our work [5] on the determination of cross sections of α-induced reactions on V, Cr and Zr is referred for the determination of these elements by CPAA.

Irradiation

Irradiation of the samples can be carried out in vacuum or air depending on the type of the sample. Both solid and liquid samples can be used in CPAA. However, solid samples are more preferable as it can withstand more particle flux. A good amount of heat is produced during irradiation and efficient cooling has to be provided in the target during irradiation to avoid melting / or decomposition of the target.

Analytical Approaches

CPAA can have both instrumental and radiochemical approaches depending on (1) level of impurity, (2) nature of impurity and (3) type of the matrix. All the classical chemical steps are used in radiochemical separation and the commonly used separation techniques are ion-exchange chromatography, solvent extraction, distillation, precipitation, etc. The chemical yield is necessary to be determined in case the separation is not quantitative.

Analytical Applications

Determinations of Low Z Elements

The major application of CPAA lies in its ability to determine the low Z elements like boron, carbon, nitrogen and oxygen even at sub ppb levels with high accuracy. This unique feature is possible because of (1) fairly large cross sections of the reactions [4] (200 to 500 mb), (2) high particle flux and (3) freedom from blank. CPAA has become a reference technique for these elements to certify the values obtained by other analytical techniques. CPAA is now routinely applied for the determination of these elements at ppm to ppb levels

Fig. 2   Detection limits of elements in CPAA

in various types of high purity materials, refractory metals, semiconductors (Si, Ge, GaAs, InP, GaP, etc.) using charged particles of proton, deuteron and α-particles.

Multi Elements by Instrumental Approach

Proton activation is ideally suited for carrying out CPAA for the multi element analysis through instrumental approach [1,6,7]. Proton energy of 10 to 15 MeV is most advantageous for the non-destructive multi element analysis. The α-particles can also be used for the trace determination of multi elements in samples by instrumental approach.

Determination of Other Elements

CPAA can be applied to determine the heavy elements [8] like platinum, thallium, lead and bismuth using proton, deuteron and α-particles. The detection limit has been reported to be in the order of 0.1 to 10 ppb. In addition. sulphur can be determined [9] in a variety of organic and inorganic matrices at trace levels. B. Constantinescu et. al. reported [10] the determination of P and Cl using proton and α-particles. It has been shown by us that CPAA can be applied to determine the rare earth elements at ppm levels in geological rock samples by α-particles using radiochemical approach.

CPAA Applications Using VEC Machine at Kolkata

Determination of Oxygen and Carbon in Metals and Semiconductors

CPAA has been applied [11] to determine oxygen in high purity materials of silicon (different grade of purity), OFHC copper (oxygen free high conductivity) and stainless steel (S.S.) samples using 40 MeV α-particles. The ^{18}F ($t_{1/2}$ = 110 min), was used for the estimation of oxygen. The instrumental approach was followed to determine oxygen impurity in Si samples (produced from rice husks for solar energy programmes) with oxygen content ≥100 ppm. It was not possible to apply instrumental approach in Cu and S.S. samples due to matrix effect. The radiochemical separation of ^{18}F was carried out by two ways, (1) distillation of H_2SiF_6 followed by precipitation of PbClF and (2) precipitation of KBH_4. The Si, Cu and S.S. samples

Table 1 - Determination of oxygen in different samples by CPAA 40 MeV α-particles, Radiochemical approach

Sample	Beam current (μamp)	Time of irradiation (hr)	Oxygen content (ppm)
A	0.8	2.0	16.7 ± 2.8
Silicon B	0.8	1.9	13.1 ± 2.7
C	0.9	2.0	22.6 ± 1.9
Silicon (p-type)	1.2	2.5	2.3 ± 0.3
	1.1	2.5	2.5 ± 0.4
Silicon (n-type)	1.1	2.5	3.1 ± 0.4
	1.1	2.5	2.8 ± 0.3
Copper (OFHC)	1.0	2.0	2.3 ± 0.3
	1.0	2.0	2.6 ± 0.3
Copper (Magnet)	0.5	0.3	380 ± 12
	0.5	0.3	370± 15
Stainless Steel	1.0	1.5	20.8 ± 2.8
	1.1	1.5	23.4 ± 2.6
Stainless Steel	0.5	0.5	151 ± 15
	0.5	0.5	162 ± 12

have been analysed using distillation technique and the results are presented in Table 1.

Carbon in Si samples was determined using 40 MeV α-particles by radiochemical approach. The product, ^{11}C [$^{12}C + \alpha = ^{11}C$ ($t_{1/2}$ = 20 min) + αn] was separated from the matrix using gas phase chemical reaction by oxidative fusion with $NaNO_3$ and NaOH. The liberated CO_2 was absorbed in strong KOH solution. The method has been standardised for the trace determination of carbon in high purity materials.

Determination of Rare Earth Elements in Geological Samples

Rare earth elements (REEs) have been determined [12] at ppm levels in geological rock samples by CPAA using 40 MeV α-particles through radiochemical approach. It has been found that REEs, Pr, Sm, Eu, Gd, Ho, Er, Tm, Yb and Lu are, in principle, possible to be determined by CPAA using α-activation. The radiochemical separation of REEs as a group was carried out from the bulk matrix where the major activities were due to isotopes of F, Na, Sc, V, Cr, Mn, Fe, Co, Ni, Ga, Ge, Zr, Nb, Mo, etc. The chemical yield of radiochemical separation varied from 65 to 80% and the time required for the separation was about 10 to 12 hrs. CPAA has been standardised for the determination of REEs in geological materials using international reference materials (Syenites), SY-2 and SY-3. The REEs determined in the above standards based on our own synthetic standard are presented in Table 2 and the experimental detection limits are also shown here.

Determination of Metals in Crude Oil

CPAA has been applied [13] for the determination of trace metals, V, Cr, Mn, Fe, Ni, Zn, Cu, Ga, present in the crude petroleum oil from north-eastern part of India. One irradiation system has been developed for loading 20 oil samples at a time and the irradiation of each sample was carried out externally in air. The standardisation process of beam energy, beam current, interferences, detection limits, has been carried out for the estimation of the above trace metals in crude oil samples.

Conclusion

CPAA is one of the most sensitive nuclear analytical technique, similar to NAA, for the determination of elements at trace and ultra trace levels in various types of materials. CPAA is routinely applied to determine the low Z elements (B, C, N, O) at sub ppb levels with high accuracy. In addition, CPAA is highly useful to determine many other elements in the periodic table, e.g., metal elements, rare earth elements, heavy metals, S, P, Cl, etc. The routine CPAA application requires a compact accelerator with desired charged particles with suitable beam energy and current.

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Table 2 - Determination of REE (ppm) in international geological reference materials by CPAA using α-particles and experimental detection limits

| REE | Synthetic Standard | International Geological reference materials | | | | Experimental detection limit* (ppm) |
| | | SY-2 | | SY-3 | | |
		This work	Reported values	This work	Reported values	
Pr	29.6 ± 0.6	21.2 ± 2.3	18.8	221 ± 21	223	0.2
		20.4 ± 2.6		205 ± 19		
		16.1 ± 1.9		195 ± 25		
Sm	33.6 ± 0.7	17.8 ± 2.3	16.1	115 ± 11	109	0.1
		14.2 ± 2.1		102 ± 13		
		14.5 ± 2.2		124 ± 14		
Eu	18.5 ± 0.3	2.7 ± 0.4	2.42	19.5 ± 2.4	17	0.02
		2.8 ± 0.3		16.9 ± 2.4		
		2.1 ± 0.4		15.6 ± 1.7		
Gd	21.5 ± 0.4	14.8 ± 1.5	17	92 ± 12	105	0.3
		16.8 ± 1.9		95 ± 10		
		14.5 ± 1.7		101 ± 14		
Ho	11.8 ± 0.2	3.3 ± 0.3	3.8	33.4 ± 3.7	29.5	0.007
		4.2 ± 0.4		31.9 ± 3.4		
		3.6 ± 0.4		30.8 ± 4.0		
Er	18.7 ± 0.4	10.6 ± 1.5	12.4	76.1 ± 6.8	68	0.06
		9.9 ± 1.2		72.5 ± 8.3		
		10.4 ± 1.3		78.2 ± 7.8		
Tm	10.7 ± 0.2	2.5 ± 0.4	2.1	13.0 ± 1.7	11.6	0.02
		2.4 ± 0.4		13.2 ± 1.9		
		1.8 ± 0.3		12.4 ± 1.7		

*Experimental detection limit based on syenites reference materials

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Ion Beam Analytical Techniques - Principles and Applications

Dr. V.S. Raju *had obtained his Master of Science in Nuclear Physics from Andhra University Waltair and joined the Training school of Bhabha Atomic Research Centre in 1974, 18th batch in the Physics discipline. He was awarded the Ph.D in 1994 from Bombay University for his studies in surface science. He had been associated with the Surface Analysis using X-Ray Photoelectron Spectroscopy, Ion Beam Analysis and the related instrumentation. Since 1994, he has been heading the Surface and Profile Measurement Laboratory of CCCM, Hyderabad. He had been leading the group to setup the state of art facilities in Ion Beam Analysis and other surface techniques and infrastructure to develop the laboratory to the acclaimed level of excellence.*

Shri Sanjiv Kumar *graduated from Training School BARC in 1987, 30th batch of Chemistry discipline. He has been involved in surface characterization of materials using ion beam analysis and X-Ray Photo electron Spectroscopy. He has been responsible for the development of Ion Beam Analysis programme of CCCM.*

Introduction

Surface and interface analysis constitutes an important aspect of material science. Ion beam analysis (IBA) has been the mainstay for investigating surface and near surface regions of materials since past three decades [1], providing a multitude of information non-destructively. It is sensitive to low as well high Z elements, irrespective of their chemical environment. It provides quantification of the major, minor and trace elements with good accuracy. It is capable of depth perception of the constituents with high resolution. Ion beams would undergo channeling in crystals when aligned with the crystal axes. All these features of IBA make it eminently suitable for elemental and compositional analysis, depth distribution, defect analysis and interfacial characterisation. Consequently it has been used for analysing ultra thin films, multi-layered structures and bulk materials as well. The areas of application of IBA, therefore, span from the state of art semiconductor technology to archaeology. The advent of ion microprobe has further expanded the scope of IBA to micron and sub micron area analysis, providing additional information [2].

Ion beam analysis techniques have been classified on the basis of the processes and the mode of detection of the associated reaction products. Nuclear reaction analysis (NRA), Backscattering spectrometry (BS), Elastic recoil detection analysis (ERDA), Particle induced X-ray emission (PIXE), Particle induced γ-ray emission (PIGE) and Nuclear microscopy are the principal ion beam analytical techniques. Each technique provides unique information and therefore is utilized for specific applications. The ion beams, obtained from a particle accelerator and impinging on a material, induce several processes simultaneously. An example of such an ion beam interaction with an aluminum target is shown in Fig. 1. Because of the small

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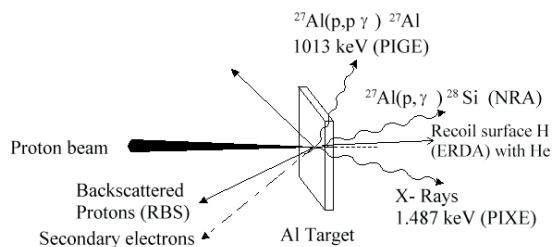
²⁷Al(p,p γ) ²⁷Al
1013 keV (PIGE)

²⁷Al(p, γ) ²⁸ Si (NRA)

Recoil surface H (ERDA) with He

Proton beam

Backscattered Protons (RBS)

Secondary electrons

Al Target

X- Rays
1.487 keV (PIXE)

Fig. 1   An example of ion beam interaction with a target of aluminium showing different interactions leading to different techniques.

Table 1 - Nuclear Reactions used in NRA

Nuclear reaction	Q-Value MeV
$^9Be(p,D)^9Be$	0.5592
$^{11}B(p,\alpha)^8Be$	8.582
$^{15}N(p,\alpha\gamma)^{12}C$	4.966
$^{19}F(p,\alpha\gamma)^{16}O$	8.1137
$^{12}C(D,p)^{13}C$	2.722
$^{14}N(D,\alpha)^{12}C$	13.574
$^{16}O(D,p)^{17}O$	1.917

analyte volume involved in each individual interaction and specificity of the type of interaction, the qualitative and quantitative analyses of surface layers upto a few microns are non-destructively characterized in any material. This article presents a brief description of the principles and applications of these techniques.

Description of Principles and Applications

Nuclear Reaction Analysis

Nuclear reaction analysis (NRA) employs a specific nuclear reaction with known reaction cross-section and Q-value. It is best suited for the analysis of low Z elements such as hydrogen and its isotopes, boron, oxygen and fluorine. It is highly selective and isotope specific. Energetic beams of protons, deuterons, α-particles, and some heavy ions such as ^{15}N and ^{19}F are used as projectiles. Some of the of t used nuclear reactions are listed in Table 1. The products in most of the reactions are charged particles and/or γ-rays. A surface barrier detector measures the charged particles, while γ-rays are measured using a suitable scintillation or semiconductor detector. High Q values and isotopic specificity allow interference and background free detection of the charged particle. Similarly, γ-rays emanating from nuclear reactions have energies more than 2.6 MeV, which is roughly the upper energy limit of the natural background radiation. It is to be noted that nuclear reactions, deuteron induced in particular, can produce neutrons. Special experimental arrangements with shielding are therefore required while performing deuteron induced NRA. The yield of the reaction products

relative to a suitable standard is used for quantification. The standard must be laterally uniform, compatible with high vacuum and stable on ion beam bombardment [3]. The depth profile measurements are based on the energy loss of the incident ion beam and that of the resultant particle. However, nuclear resonance reaction analysis (NRRA) provides depth profiling with better resolution, sometimes in the range of tens of Å. The depth profiling is performed by increasing the incident ion beam energy beyond the resonance energy in suitable steps and measuring the corresponding yield.

The determination of hydrogen on materials surfaces is one of the most important applications of NRRA. The determination and depth profile of hydrogen is carried out using $^1H(^{15}N, \alpha\gamma)^{12}C$ and $^1H(^{19}F, \alpha\gamma)^{16}O$ reactions having resonances at 6.38 and 6.46 MeV respectively. The measurement of high energy γ-rays is preferred to α particles. The sensitivity of the reaction is about 2000 atomic ppm and probing depth about 2 to 3 microns. The reaction $^1H(^{15}N, \alpha\gamma)^{12}C$ provides a depth resolution of about 30 Å (Si) where as $^1H(^{19}F, \alpha\gamma)^{16}O$ reaction would provide about 200 Å (Si) depth resolution. Some of the applications of this method include determination of hydrogen in Nb_3Ge superconductors, films of silicon nitride, porous silicon layers and structural materials like SS and zirconium alloys [4,5]. The depth profile of hydrogen in about 5500 Å thick film of silicon nitride obtained using $^1H(^{19}F,\alpha\gamma)^{16}O$ resonance reaction is given in Fig. 2. The average content of hydrogen in the film is around 20%. The reaction $^1H(^{15}N, \alpha\gamma)^{12}C$, due to its excellent depth resolution,
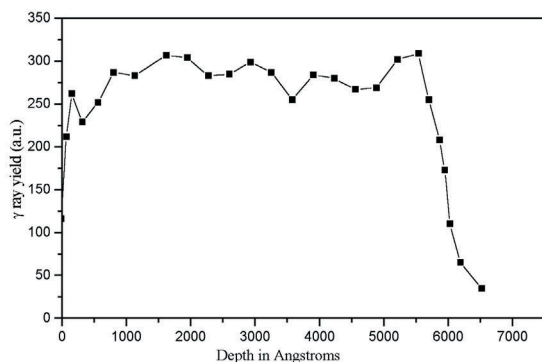
Fig. 2   Depth profile of hydrogen in a thin film of silicone nitride on GaAs obtained by $^1H(^{19}F,\alpha\gamma)^{16}O$ nuclear resonance reaction

has been used to study the diffusion of hydrogen in several metals and alloys. These reactions are sensitive only to ^1H. The other isotopes of hydrogen, deuterium and tritium are determined using $^2H(^3He, p)^4He$ and T(d,n) reactions respectively.

The inverse reactions, $^{15}N(^1H, \alpha\gamma)^{12}C$ and $^{19}F(^1H, \alpha\gamma)^{16}O$, have been extensively used earlier for the determination of nitrogen and fluorine in a variety of materials. The properties of several materials such as thin oxide films and 123 superconductors depend considerably on their precise oxygen content and NRA has been used for the precise determination of O in these materials.

Backscattering Spectrometry

Rutherford backscattering spectrometry is the most versatile and widely used ion beam analytical technique [6]. It is based on the classical gold foil experiment of Rutherford. It involves (a) measurement of energy and (b) yield of ions backscattered from the atoms in the near surface region of materials. Accordingly, the concepts of two parameters namely Kinematic Factor and differential scattering cross section related to the energy of the backscattered ions and their yields respectively are pivotal in backscattering spectrometry.

Kinematic Factor

The process of backscattering is elastic and Coulombic in nature. The ratio of energy E of the ion backscattered from a target atom to the incident beam energy E_0 is known as kinematic factor, K. It is a function of the masses of the projectile and target and the backscattering angle, and is always less than unity. It provides identification of the elements constituting the target on the basis of their masses; its value being the highest for the heaviest element. RBS is a multi-elemental technique. The mass resolution depends on the energy resolution of the detection system but can also be improved by increasing the Z and energy of the incident beam and backscattering angle.

Differential Scattering Cross Section

The yield of the backscattered ions from a specific element depends on the scattering cross section. The scattering cross section for an element is directly proportional to the square of the atomic numbers of the projectile and the target element and inversely proportional to the square of the incident beam energy. It is also a function of backscattering angle. It is calculated accurately using the standard expression for Rutherford backscattering cross section. This feature of RBS allows the determination of the atomic composition of a multicomponent target without any standards. The depth scale is established on the basis of the energy loss of the incident ion beam and that of the backscattered ions in the material. This enables the determination of thicknesses of films and concentration profile of elements in diffusion experiments.

RBS is usually performed with 2.0-2.5 MeV α-particles. However heavy ions such as ^7Li and ^{12}C in the energy range of 6 to 12 MeV are being increasingly used. They provide better mass resolution, isotopic discrimination and enhanced backscattered yield. RBS is less sensitive to low Z elements and more sensitive to high Z elements. The detection sensitivity for O on Si by 2 MeV α-RBS is about 4×10^{14} atoms cm^{-2} whereas that for Au on Si is about 10^{12} atoms cm^{-2}. However, the excitation functions of 1- 4 MeV proton and α-particles for scattering from low Z elements such as C, N, and O exhibit, in deviation from the Rutherford
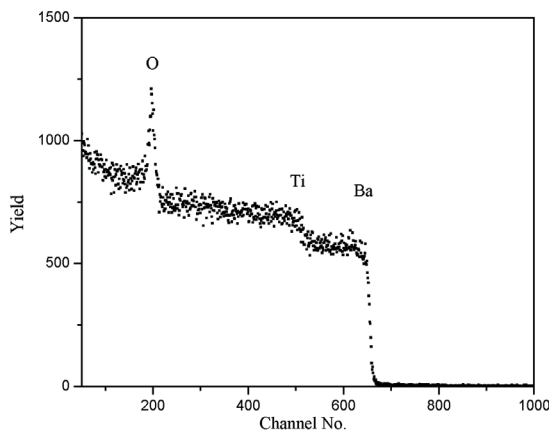
Fig. 3 $^{16}O(\alpha,\alpha)^{16}O$ resonance scattering from
          barcium titanate at 3.05 MeV

Fig. 4   Proton backscattered spectra from silicon
          nitride films on (a) GaAs and (b) Silicon
          $E_F = 2090$ keV

backscattering cross section, distinct abnormalities
[7,8]. These are characterized by resonances with
scattering cross-sections several times higher than
corresponding Rutherford values. In addition,
nuclear backscattering (NBS) or non-Rutherford
backscattering enhances the scattering cross sections
due to nuclear interactions. For example, the
$^{16}O(\alpha,\alpha)^{16}O$ scattering has a resonance at 3.05 MeV.
The width of the resonance is about 10 keV and has
about 22 times higher cross section [8]. This
resonance scattering enhances the detection
sensitivity of oxygen by ten times.

It has also been used to study surface relaxation
and reconstruction, growth of epitaxial layers,
analysis of buried layers, diffusion across interfaces
and other aspects related to surface, interface and
thin film technology [9]. The combination of RBS
and channeling has been used for defect analysis in
crystalline materials. High resolution RBS, with
typical depth resolution in the range of several Å,
enables the analysis of ultra thin films and
multi-layered structures. $^{16}O(\alpha,\alpha)^{16}O$ scattering,
described earlier, has been used for the
determination of O in superconductors and other
perovskite materials [10]. The backscattered
spectrum from barium titanate, a perovskite
material, resulting from 3.05 MeV $^{16}O(\alpha,\alpha)^{16}O$
resonance scattering is shown in Fig. 3. $^{16}O(p,p)^{16}O$
scattering has been used to determine the thickness
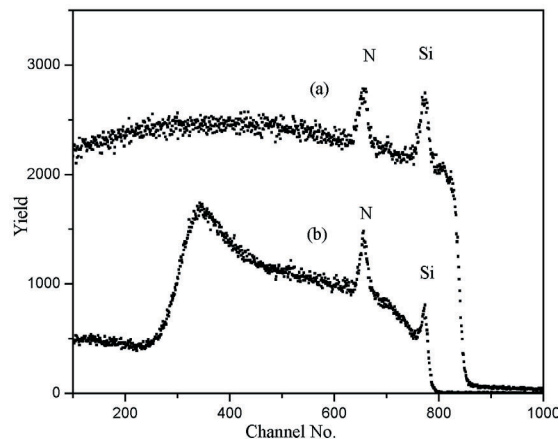of zirconium oxide layers on autoclaved zircaloy

[11]. This scattering has been found to be superior to
$^{16}O(\alpha,\alpha)^{16}O$ scattering for determining the overall
composition of thicker films. Similarly, $^{14}N(p,p)^{14}N$
is extremely useful for analysing films of silicon
nitride, chromium nitride and ternary nitride
coatings [12]. The applicability of this scattering for
the compositional analysis of such films is amply
demonstrated by Fig. 4.

Elastic Recoil Detection Analysis (ERDA)

ERDA is a simple and very useful IBA
technique for depth profiling of light elements. The
physical concept governing ERDA is identical to
RBS [13]. It involves the bombardment of target
with ion beam and the detection and energy analysis
of the recoils form the target in the forward direction.
A particle filter of suitable thickness is placed in
front of the recoil detector to prevent the ion beam
scattered in the forward direction from being
counted. ERDA like RBS invokes the concepts of
kinematic factor, differential scattering cross section
and energy loss. The energy straggling of the recoils
in the filter introduces statistical fluctuations in the
energy loss limiting the depth resolutions. ERDA
has also simultaneous multi-element detection
capability. Atoms of different elements recoiled
from the surface appear at different energies.
However in contrast to RBS where signals from light
elements appear at low energies and heavy elements
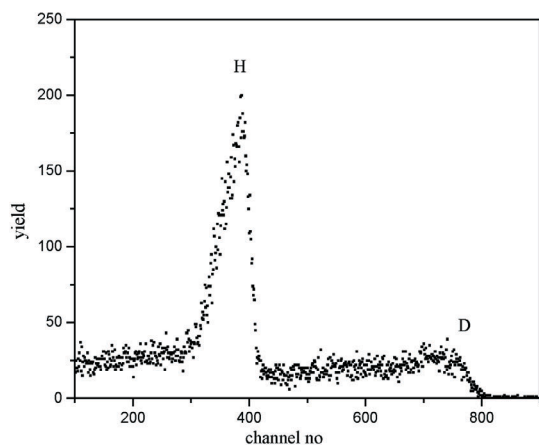at higher energies the energy of the detected recoils

Fig. 5   ERDA spectrum from a zircaloy coupon charged with hydrogen and deuterium with 6 MeV ^{12}C beam

of different masses depend on the stopping power and thickness of the stopper foil.

The energy of the incident ion beam for ERDA is usually ~ 1 MeV/ amu. The use of high-energy heavy ions such as Cl enables the determination of low Z elements. However the determination of hydrogen and its isotopes is the main application of ERDA using low energy particle accelerator (Fig. 5) in ERDA, 3-5 MeV α- particles and 8-10 MeV ^{12}C ion beam are frequently used. Beam induced desorption of hydrogen is less in α- ERDA compared to heavy ion ERDA or NRRA. The detection sensitivity and probing depth of ERDA are similar to NRRA but this technique is fast for depth profiling measurements.

ERDA has found applications in the analysis of porous silicon layers, diamond like carbon (DLC) films, silicon nitride and silicon oxynitride films [14]. In some cases the composition of the films has been determined on the basis of single measurement.

Particle Induced X-ray Emission (PIXE)

Particle induced X-ray emission analysis is used for the determination of minor and trace elements in a matrix. It involves the bombardment of the matrix preferably with 2.0 – 3.0 MeV proton beams and measurement of characteristic X-rays,

resulting from the interaction of the beam with the target elements [15]. The energy of the characteristic X-rays is unique for an element. Therefore the elements are identified on the basis of their characteristic X-ray energies. The X-rays are measured with semiconductor detector.

The creation of a vacancy in one of the core levels of an element by the ion beam and its subsequent decay with the emission of characteristic X-rays summarises the physical process involved in PIXE. The first step corresponds to ionization cross-section and the second to fluorescent yield. The shell ionization cross section increases with decrease in Z of the element while the fluorescent yield increases with increase in Z. The inner shell ionization cross section also increases with incident beam energy. α-particles and other ions of suitable energy can also be used as probes in PIXE experiments. However the background associated with these ions is more pronounced relative to proton beam thus limiting their applicability.

PIXE has been classified in two categories depending on the thickness of the targets. PIXE normally refers to thin targets. The proton beam loses negligibly small energy while traversing it. The thickness of such targets is about 50-100 μg cm^{-2}. The targets are generally prepared on thin backing materials like Mylar or Nucleopore filters [16]. Evaporation, spraying, filtering are some of the generally used processes for the preparing thin targets. Though the preparation of thin targets is rather tedious, the related quantification is much easier. The concentrations of elements are determined using sensitivity curves constructed using thin external standards. The elements can also be quantified relative to a single internal standard added to the thin target itself.

In thick target PIXE (TT-PIXE), the thickness of target is such that the beam loses all its energy in it. In contrast to regular PIXE, though the preparation of thick targets is easier, quantification is difficult. It is due to matrix effects. Firstly, the ion beam while traversing the specimen loses energy continuously. Therefore the production of X-rays also varies with depth. Secondly, the X-rays generated deeper inside the target get attenuated in the overlying layers before their detection. The quantification of minor
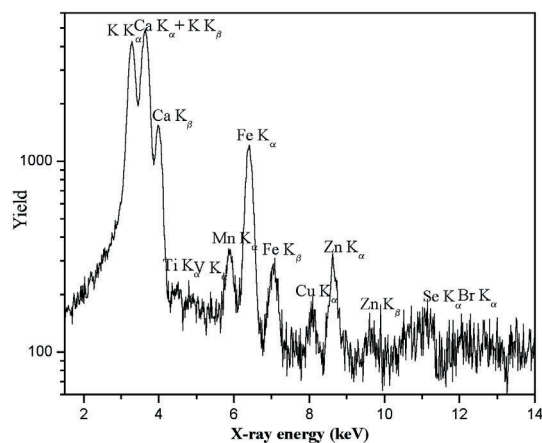
Fig. 6   PIXE spectrum of a medicinal plant (Mentha Arvensis)

Table 2 - Reactions used in PIGE

Element	Nuclear Reaction	Energy of γ-ray. keV
Li	$^7Li(p,p\gamma)^7Li$	478
B	$^{10}B(p,p\gamma)^7Be$	431
F	$^{19}F(p,p\gamma)^{19}F$	110.197
Na	$^{23}Na(p,p\gamma)^{23}Na$	440
Mg	$^{25}Mg(p,p\gamma)^{25}Mg$	585
Al	$^{27}Al(p,p\gamma)^{27}Al$	1013
Si	$^{29}Si(p,p\gamma)^{29}Si$	1779
P	$^{31}P(p,p\gamma)^{31}P$	1266
S	$^{32}S(p,p\gamma)^{32}S$	2237

and trace elements by TT-PIXE requires a priori knowledge of the composition of the specimen. The authors have developed a TTPIXE calibration approach for such specimens. This method requires a priori knowledge of the concentration of any two elements appearing in the X-ray spectrum of the specimen [17].

PIXE is suitable for the determination of elements with Z> 15. This technique allows the determination of most of the elements down to ppm levels with an accuracy of about 10 %. The trace element estimation capability of this technique has been exploited for studies in several fields such as biology and medicine, geoscience, atmospheric pollution, art and archaeology. Art objects and archaeological specimens, which are too large to be accommodated in scattering chamber and samples that cannot withstand vacuum, are analsyed by in air PIXE [15]. The PIXE spectra for a medicinal plant specimen is given in Fig. 6.

Particle Induced γ-ray Emission (PIGE)

Particle induced γ-ray emission (PIGE) involves measurement of prompt γ-rays emanating from a nuclear reaction induced by the incident ion beam using high resolution detectors [18]. Prompt γ-rays can originate from a number of different types of nuclear reactions namely (p,pγ), (p,αγ), (p,n) and (p,y). This technique provides sensitive determination of several low Z elements such as B, Li, F, Na, Al, Mg and Si. Therefore this technique is complementary to PIXE. A combination of PIXE and PIGE would enable the determination of several elements across the periodic table. A list of elements along with reactions and γ-rays suitable for analysis by PIGE are given in Table 2.

PIGE measurements are usually carried out with 3-5 MeV proton beam. The target is in the form of pellet. PIGE is devoid of pulse pile up problems generally encountered in PIXE and produces totally different spectra for elements of neighboring Z. High resolution γ-ray spectrometry makes the spectral analysis easier. In order to use prompt γ-ray emission as a means of multi-element analysis of a complex material, it is imperative to know the thick target yields of γ-rays for pure elemental samples. This would also help in ascertaining interferences, if any.

Though this technique has enormous potential for the determination of low Z elements, it is yet to receive widespread recognition compared to PIXE. However, this technique has been extensively used in our centre for a variety of applications. Some of applications include analysis of kidney stones, determination of F and other elements in bio-monitors for pollution, analysis of F in minerals used in television manufacturing industries and elemental analysis in medicinal plants. A PIGE spectrum of a medicinal plant is shown in Fig. 7.
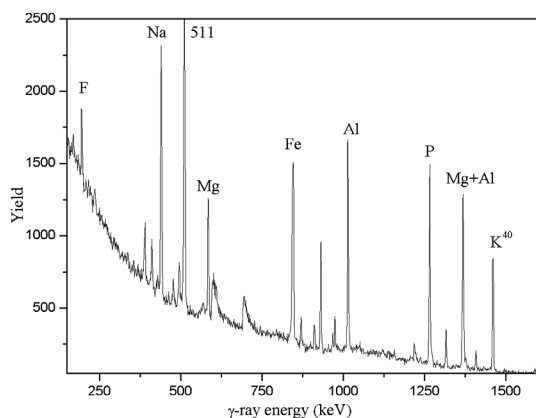
Fig. 7   PIGE spectrum of a medicinal plant (Dactyloctenium Aegypeticium)

Nuclear Microscopy

The advent of nuclear microscopy or ion microprobe analysis has added a new dimension to IBA [2]. The beam in conventional IBA is usually 1-2 mm in diameter. In nuclear microscopy, ion beams of micron and sub micron dimensions are scanned over a specimen to provide spatial information. The formation of micron and sub micron dimension beams involves demagnification of an object aperture measuring in the range of 10-100 microns by means of a magnetic or electrostatic focusing system [19]. The combination of high spatial resolution and the inherent depth perception capability of IBA makes nuclear microscopy an ideal technique for three-dimensional elemental mapping.

All the ion beam analytical techniques discussed earlier can be performed using the ion microbeam. These can be used to ascertain the micro homogeneity of materials, locate inclusions and study interfacial or grain boundary segregation. For example, elemental map obtained by μ-PIXE in Fig. 8 provides the positional information of a GaAs particulate on a crystal of Si. Similarly the elemental micro inhomogeneity in a biological material is demonstrated in Fig. 9. μ-PIXE has been extensively used in environmental, biological and biomedical research. The elemental microanalysis of tissues and cells have been carried out to investigate the role of trace elements like Al, Ca in Parkinsons and Alzheimers diseases. In addition, techniques like scanning transmission ion microscopy (STIM), ion beam induced charge collection (IBIC), single event upset studies are exclusively based on ion microbeam [20]. These techniques have been extensively used in semiconductor technology. The information provided by these techniques can be used to study single event effects in operating integrated circuits, charge collection efficiency in
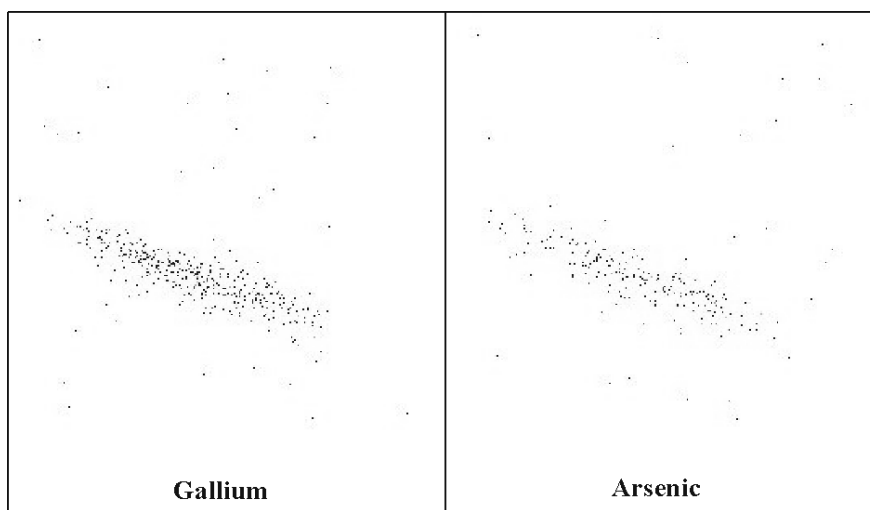

Fig. 8   Micro PIXE elemental maps of a gallium arsenide particle on a silicon wafer (Scanned area 800 X 800 square μm)
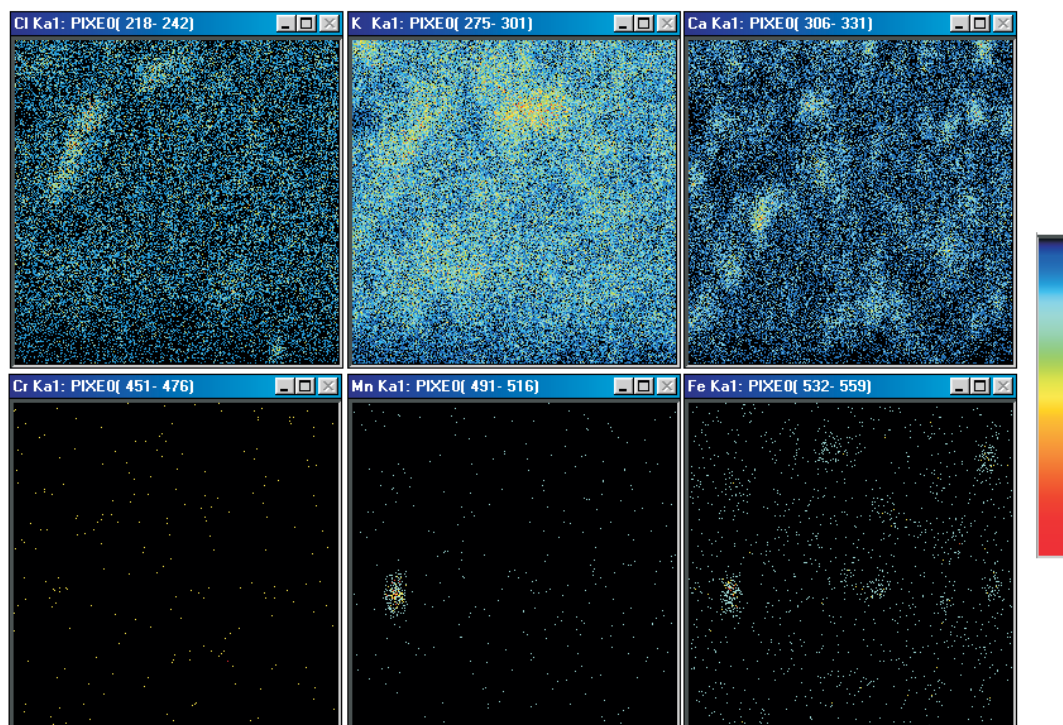
Fig. 9   Micro MIXE elemental maps (1250 x 1250 microns) of Cl, K, Ca, Cr, Mn and Fe in a biological sample (200 mesh size)

radiation detectors that contain defects or other non-uniformities, and radiation damage.

Experimental Arrangement

In this section, the experimental arrangement required for IBA is briefly discussed. The ion beam experiments are carried out in scattering chambers, situated at the end of a beam line, where the ion beam emerging from accelerator impinges on the target and the reaction products are detected. The beam currents for regular IBA techniques are few nanoamperes, while about 100 pA currents are used in ion microprobe analysis. The beam line is equipped with beam steerers, beam profile monitors and beam defining collimators.

The specimens to be analysed are mounted on a sample manipulator and introduced into the scattering chamber. The scattering chamber has provisions for current measurement and secondary electron suppression. The design of scattering chamber is unique for a given ion beam technique.

For example, PIXE chambers are lined with graphite foil to minimize the probability of nuclear reactions occurring when the scattered protons strike the walls of the chamber. Similarly the chamber has provisions for placing the detector at 90 or 135 degree relative to the beam direction, the normal detection geometries for PIXE. The choice of materials for collimators, specimen holders and Faraday cups is also crucial. Generation and maintenance of high vacuum of the order better than 1×10^{-6} mbar all along the beam path is very essential. The beam lines should be preferably pumped by turbomolecular pumps for a clean vacuum to avoid the contamination of targets with adventitious hydrocarbons.

The data acquisition is performed in optimized geometry using standard electronic gadgets to yield spectra with good signal to noise ratio. Standard ion beam analysis software packages like GUPIX (PIXE), GISA and RUMP (RBS, ERDA) are useful in the spectral analysis.

Ion beam analytical laboratories with these features are required for solving problems arising in different fields of research and industry. The Surface and profile measurement laboratory at C.C.C.M./B.A.R.C. at Hyderabad is one such laboratory equipped with many ion beam analytical techniques, besides its competence in ultra trace level analysis.

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Radiotracers in Separation

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The advent of new generation reactors and accelerators has provided easy access to 'carrier-free' radioisotopes of most of the elements in the periodic table. This, in turn, has led to extensive applications of radioisotopes as tracers for studying various separation/ preconcentration processes used in analytical science and waste management. In general, radiotracers are used in separation science to optimize chemical conditions required at different stages of separation process. Radiotracer is used as a probe for evaluation of separation efficiency as a function of various operating parameters. Radiotracers have also been used for basic understanding of separation processes such as selectivity, extraction / ion-exchange kinetics, isotherms and diffusion mechanism. There are several factors that make radiotracer as an ideal analytical tool for developing viable separation process. For example, routine radioanalytical techniques allow detection of quantities that are 10^5 times smaller than those needed for chemical analysis. Interference from other species, that may be present, is not important in radioanalytical techniques as compared to conventional methods of analysis where interferences may thwart the analysis. Therefore, sample manipulations are minimum in the measurements of radiotracers.

Georg Hevesy, Noble Prize winner in 1943, was first to use radiotracer (^{210}Pb) for determining the solubility of lead salts in water. Radiotracer can be used either qualitatively, as simple markers of a process, or quantitatively, to determine the amounts of non-radioactive species. Radiotracers are ideal markers because of the fact that radioactivity is not affected by physico-chemical state of the system. Equilibrium processes that can be studied using radiotracers include self-diffusion in solids, mass transfer in liquids, isotope exchange reaction and complex formation.

Discovery of artificial radionuclides by I. Curie and F. Joliot provided the impetus to radiotracer applications in separation science because radiotracer could be produced to fit specific needs.

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List of commonly used radiotracers in separation science is given in the Table 1. In principle, all the modes of radioactive decay can be used for analysis of radiotracers. However, γ-emitting radiotracers are most preferred for studying separation processes. The choice of γ-emitting radiotracers is related to the fact that no special sample preparation method is required and radiochemical purity is not essential for measurements using HPGe detector coupled with multi-channel analyzer. Short-lived radiotracers offer advantage that they can decay away at the conclusion of the experiment and leave an essentially "non-radioactive" mixed system for further use, in addition to minimising radioactive waste management. However, measurement of short-lived radiotracer requires appropriate decay corrections. Also, the radiotracer should not be too short-lived to decay during experiment itself. This becomes pertinent in the experiments that do not involve rapid equilibrium. It should be noted that reference radiotracer standards are required for quantitative analysis of radiotracers. The exact amount of radiotracer is also required in many applications. This is not a problem if carrier-free radiotracer is used or the knolwedge of the concentration of inactive material presses with the tracer.

Appropriate safety consideration must be followed during the handling of radiotracer. All radioactive material can be hazardous if they are not handled correctly. Physical handling of low-level radioactive material can be carried out inside a fume hood connected to an exhaust system and using disposable latex gloves.

Some General Considerations

In general, the applications of radiotracers in separation science utilize the assumption that radioactive material will blend perfectly with the system under study. This means that the radioactivity emitted by the tracer will not adversely affect any components of the system, and that the radiotracer will behave in a way that is indistinguishable from the non-radioactive materials, except for emitted radiation. It is important to note that most of the separation systems involves organic components which are not very resistant to radiation. Fortunately, the excellent sensitivity of most radioactivity assay methods minimizes the need to employ radiotracer dose of such a magnitude that any detectable radiation damage occurs. Most importantly, the radiotracer and the stable nuclide must undergo isotopic exchange. It is expected that during production of radiotracer, Szilard-Chalmers effect may change the chemical state of radiotracer thus produced. Hence, one must ensure that the radiotracer atoms and their corresponding stable atoms must be in the same redox state. The isotopic effects (combination of kinetic, entropy and energy effects) may become relevant particularly for elements of low atomic weight (< 25) and appropriate considerations for this effect must be taken into account in specific applications [1].

Chemistry of Radiotracers

For a reversible chemical reaction using tracer, T and reactant, R leading to the product, P the reaction equilibrium is

$$tT + rR \leftrightarrow pP$$

and the free energy of reaction is

$$\Delta G = \Delta G^\circ + RT \ln \frac{\{P\}^p}{\{T\}^t \{R\}^r}$$

where the braces indicate activities of the substances involved. For a chemical equilibrium, this is reduced to

$$\Delta G^o = -RT \ln K$$

where K is the equilibrium constant. It is obvious that the equilibrium constant can be different when macroscopic quantities are replaced by microscopic quantities such as the carrier free radiotracers. The higher tendencies of radiotracers to hydrolyze and polymerize is a well known phenomenon. However, this can be minimized by the suitable addition of carriers.

Another factor one needs to take care of while using radiotracers is the suitable choice of pH which, if exceeded, can onset the formation of radio colloids. If the solution contains polymeric material arising due to the hydrolysis of the metal ions, they also tend to sorb the radiotracers. These processes are called radio colloid formation and can affect the

Table 1 - Some of the Commonly Used Tracers

Nuclide	Method of production[*]	Half-life	Decay mode: Energy[#] (MeV)
^{3}H	R	12.33y	β^{-} : 0.018
^{14}C	R	5730y	β^{-} : 0.156
^{22}Na	C	2.6y	β^{+}, γ : 1.274
^{24}Na	R	15.0h	γ: 1.369
^{32}P	R	14.3d	β^{-}: 1.71
^{33}P	R	25.3d	β^{-}: 0.249
^{35}S	R	87.4d	β^{-}: 0.169
^{36}Cl	R	3.0×10^{5}y	β^{-}: 0.71
^{45}Ca	R	162.6d	β^{-}: 0.257
^{47}Ca	R	4.54d	β^{-}: 1.99; γ: 1.297
^{51}Cr	R	27.7d	γ: 0.32
^{54}Mn	R	312d	γ: 0.835
^{59}Fe	R	44.5d	γ: 1.292, 1.099
^{60}Co	R	5.27y	γ: 1.173,1.332
^{63}Ni	R	100.1y	β^{-}: 0.067
^{65}Zn	C,R	244.3d	γ: 1.116
^{75}Se	R	119.8d	γ: 0.265, 0.136
^{85}Sr	R,C	64.8d	γ: 0.514
^{86}Rb	R	18.6d	β^{-}: 1.77
^{99}Mo/^{99m}Tc	F	65.9h/6.01h	γ: 0.143
^{106}Ru	F	373.6d	β^{-}: 0.039
^{109}Cd	C	461d	γ: 0.088
^{110m}Ag	R	249.8d	β^{-}: 3.0
^{111}In	C	2.8d	γ: 0.171
^{125}I	R	59.4d	γ: 0.035
^{131}I	R	8.02d	β^{-}: 0.606; γ: 0.365
^{137}Cs	F	30.1y	γ: 0.662
^{153}Gd	R	240.4d	γ: 0.103
^{201}Tl	C	72.9h	γ: 0.167
^{210}Pb	R	22.3y	β^{-}: 0.017,0.064

* R: reactor, C: cyclotron, F: fission, # β energy = β_{max}

chemical state of the radiotracer in the solution. In order to avoid the formation of radio colloids the pH must be kept as low as possible and any particulate matter need to be filtered out. The radioactive tracers do adsorb on the surface of the container (such as glass, plastic also and clay) especially at a pH higher than where the hydrolysis occurs [2]. It has been reported that the radiotracers also sorb onto particulate matters such as precipitates, suspended particulates, dust, cellulose fibres, glass fragments, and organic materials.

Applications in Separation

Radiotracers are used in chemical separations like solvent extraction, precipitation, ion exchange, chromatography or membrane based separation methods. The separation may be required from a large variety of diverse elements as in the case of fission product analysis, or from neighboring elements in the periodic table, as in procedures for targets bombarded by low energy (a few MeV) nuclear particles. In many cases, interfering activities must be reduced by a factor of 10^4 to 10^6 or more although the yield of the desired activity need not be quantitative. Some of the applications of radiotracer in separation science are described below:

Preconcentration

A problem of paramount importance in analytical chemistry is selectivity, particularly at low analyte concentrations in the presence of interfering substances. Direct determination of metal traces in various samples usually requires an efficient preconcentration step in order to bring the concentration of the analyte within the dynamic measuring range of the detector and enhances the sensitivity to sub-ppb level. Additionally, the preconcentration step provides differentiation of different chemical forms of the element and also eliminates matrix effects and interferences that cannot be manipulated by the measuring device. Conventional separation and preconcentration techniques such as co-precipitation, distillation, liquid-liquid extraction, ion-exchange and absorptive columns have been employed for the single- or multi-element extraction of almost every metal from their initial matrices [3]. However, these preconcentration / separation methods require a very

sensitive method for establishing a reliable methodology for determination of target element. Radiotracers offer such possibilities because they can be used under dynamic conditions with minimum sample manipulation and provide higher degree of sensitivity. For example, 2-mercaptobezothiazole loaded Bio-beads SM-7 resin was applied to the separation and preconcentration of inorganic and alkyl mercury species for their atomic absorption spectrometry determination in natural waters [4]. The test of this proposed analytical method was carried out using ^{197}Hg radiotracer. There are many such examples which highlight the importance of radiotracer in establishing reliable preconcentration methodologies.

Apart from this, radiotracer ions are extensively used to measure the exchange capacity of sorbents. The capacity of a polymer inclusion sorbent (PIS) prepared for Cr(VI) uptake was determined using ^{38}Cl radiotracer (37.2 min) [5]. The amount of Cr(VI) present in the samples was obtained by using ^{51}Cr (27.7 d) radiotracer. The abundances of $HCrO_4^-$ and CrO_4^{2-} in the sobent were estimated by charge balance. The comparison of abundances of $HCrO_4^-$ and CrO_4^{2-} in the samples and aqueous solutions at different pH is shown in Fig.1. It is evident from Fig.1 that there is an excellent correlation of species of Cr(VI) present in the PIS with that expected in the aqueous medium. Similar concept is used for estimating the selectivity of competing ions / species in separation system.

Precipitation

Many separation methods involve precipitation using a radiotracer and a carrier solution. The tracers due to their low concentration usually can not be precipitated. They, however, can be precipitated using a carrier solution which scavenges the isotope of interest. This has a serious drawback as sometimes other radionuclides of similar chemical nature get scavenged. This is often termed as co-precipitation. The choice of carrier for the precipitation or co-precipitation depends on nature of metal ion, nature of anion, medium of precipitation, solubility product of the cation and anion of interest. Isotopic exchange is one of the main processes in the application of radiotracers in separations by precipitation. For example, the
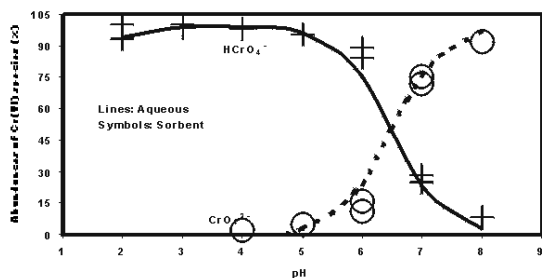
Fig. 1   Variation of Cr(VI) species in the aqueous solution and held in PIS formed by immobilizing Aliquat-336 in the matrix formed by cellulose triacetate and 2-nitrophenyl octyl ether.

exchange of silver ion between a precipitate of silver chloride and a solution of silver nitrate reaches isotopic equilibrium rapidly. Because of the low solubility of silver chloride, a very favourable ratio exists at equilibrium between the silver species in the precipitate and in the solution. For this reason, if AgCl is added to a solution containing only a trace amount of radioactive silver, a high percentage of this radioactive silver will have exchanged with the silver in the precipitate by the time equilibrium is attained. This aspect has been made use of to develop a rapid, high decontamination, single-step method for the separation of traces of radioactive silver from a solution containing other radioactive species [6].

Radiotracers are also used for scavenging or co-precipitation. Scavenging involves formation of a bulky precipitate to remove as many active contaminants as possible from solution by co-precipitation and adsorption. The scavenging element may already be present as one of the contaminating activities or it may be a completely different element. Unfortunately, while removing the unwanted elements, some of the elements of interest also are lost. Therefore, one needs to take a judicious decision while selecting a co-precipitation method.

Ion-exchange

Organic polymers containing acidic or basic functional groups are popularly being used in separation sciences as organic ion-exchangers. The amount of material sorbed onto the resin depends on resin parameters such as extent of cross linking, particle size and nature of the functional group as well as on solution parameters such as nature of the metal ion, ionic strength of the solution and temperature. Radiotracers have been used in ion-exchange methods for the monitoring of separation efficiency by experimental variables such as pH and eluent volume.

The radioactive metal ion is sorbed at the top of the column containing the ion exchange resin (either cation or anion exchanger depending on the nature of species). The elution may be subsequently accomplished by the use of another metal ion (with higher affinity towards the resin) or a complexing agent. As the use of radiotracers utilizes only a minute fraction of the resin capacity, the separation can be achieved using a relatively miniaturized column. Subsequently, the eluent solution is passed through the column and the eluted fractions (collected in different sample vials) are counted for the radioactivity. This is a simplified mode of operation and the decontamination from the impurities can be estimated by counting the activity of the product as well as the impurities before and after the separation stages.

A typical example is the separation of trivalent lanthanides and actinides by cation exchanger DOWEX 50. The elution using alpha-hydroxy isobutyric acid was used for the effective separation of lanthanides and actinides (Fig. 2) [7].

Solvent Extraction

Radiotracers are used in solvent extraction for the easy monitoring of the process where aliquoting of the samples is immediately followed by counting of the radionuclide. This way, the process evaluation is much faster compared to the conventional assaying methods such as titrimetry or spectrophotometry where the assaying process is quite lengthy and time consuming. Radiotracers can be utilized for studying the kinetics of a solvent extraction separation process, as the rate of extraction can be obtained by using a programmed auto sampling unit which can remove aliquots at different time intervals and count the radioactivity on-line. In fast separation processes, the use of radiotracers becomes even more relevant. One particular example is the use of an automated rapid
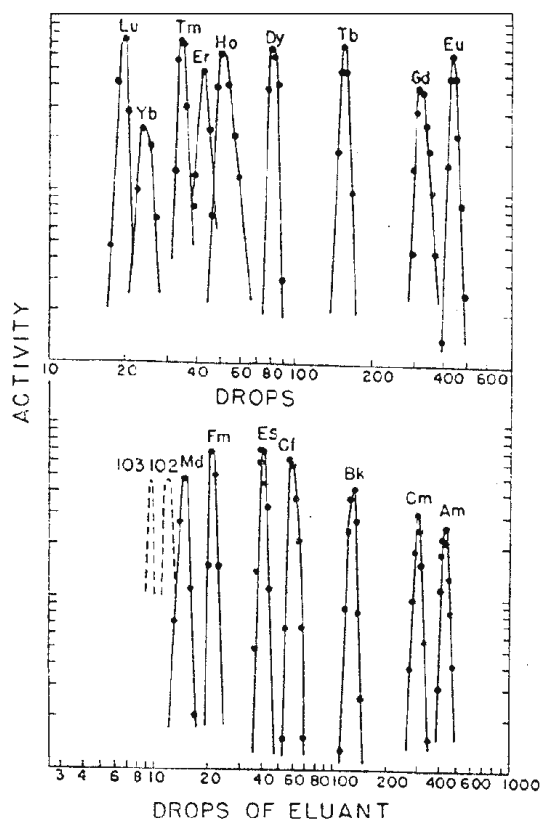
Fig. 2 *The elution of trivalent actinide and lanthanide ions using DOWEX 50 resin and alpha hydroxy isobutyrate as the eluent.*

solvent extractor developed in Sweden which is termed as AKUFVE. The instrument makes use of radiotracers to its advantage as the rapid extraction is followed by high speed centrifugation and on-line detection of the radioactivity using gamma / alpha counters. These state-of-the-art techniques which are not limited by the short half lives of some of the radionuclides make separation studies much more convenient and exciting at the same time.

Membranes

Membranes based processes such as dialysis, electrodialysis and facilitated transport. have many advantages over conventional separation methods. The diffusion process plays an important role in the separations involving membranes. The radiotracers are being used extensively for studying the diffusion mechanism across the membranes. By using radiotracer, it is possible to determine the amounts of diffusing species (counter ions and eventually co-ions) inside the membrane and to measure the self-diffusion flux of ions crossing the membrane without any driving force. The self-diffusion coefficients of the diffusing species are important parameters to understand their interaction with the membrane. The self-diffusion coefficients of ions in the membrane marked by radiotracer has been found to correlate with the selectivity coefficients of ions in the Nafion-117 membrane [8], (Fig. 3). There are many techniques such as radiotracer method, ion-exchange and conductivity measurements. which can be used for measuring the self-diffusion coefficient. While radiotracer measurements yield the well-defined ion self-diffusion coefficient, the relationship between the conductivity or the ion-exchange rate and the ion-diffusion coefficient is not straightforward. In former case, a correction must be applied for the convection conductivity arising from the electro-osmotic pore fluid flow. However, this contribution is often ignored. Another problem is that the conductivity measurements are associated with the electrical current flow through the polymer, which can induce a change in its transport properties. For example, the proton diffusion coefficient in Nafion evaluated from polarization measurements and corrected for the convection contribution ($> 8x10^{-6}$ cm^2/s) is considerably higher than the proton self-diffusion coefficient ($3.5x10^{-6}$ cm^2/s) obtained by the radiotracer method. On the other hand, the evaluation of ion-diffusion coefficient from kinetic measurements of ion exchange between a polymer membrane and the electrolyte solution is complicated by the necessity to consider the coupling between the two ion-transport fluxes. These are a few examples that demonstrate the importance of radiotracers in understanding the membrane phenomenon.

Thin Layer Chromatography

Thin layer chromatography (TLC) is an extremely useful technique where the radiotracers are successfully used for a separation process. Such methods often involve the separation of complexed (RS) and uncomplexed (S) metal ions using a particular receptor(R) molecule. As there is
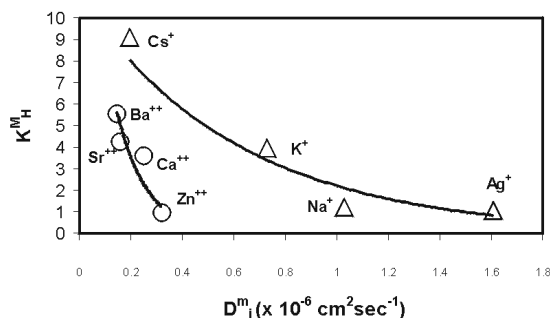
Fig. 3 *Selectivity coefficient as a function of self-diffusion coefficient of monovalent and divalent ions in the Nafion-117 membrane.*

significant difference in the mobility of the S and RS species, they can be scanned by radiographic imagers to evaluate the efficiency of the separation. Alternatively, different regions of the TLC plate can be cut and counted. The separated substance can be quantitatively recovered by leaching out the substance from the spot of interest. A few drops of the solution containing the R, S and RS mixture is usually placed in a special TLC plate and dipped in a solvent mixture that can efficiently transport only the RS species leaving behind the R and S species. Often the complex formation constants for a particular receptor molecule with a metal ion of interest is calculated by varying the pH, receptor concentration, ionic strength and temperature of the reaction mixture.

Similarly, for a mixture of organic compounds, the effectiveness of the separation process can be evaluated by tagging a radioisotope such as ^{14}C. A 2D chromatogram of the photosynthesis products of spinach cells is shown in Fig.4 after growing in $^{14}CO_2$ atmosphere. The different components with different mobilities are well segregated using the suitable eluents. Currently, the radiographic imaging technique involves storage phosphor screen imaging as compared to the traditional film autoradiography.

Conclusions

Radiotracers offer wide range of possibilities in characterization of separation processes. Radiotracers yield well-defined information which are essential for basic understanding of separation
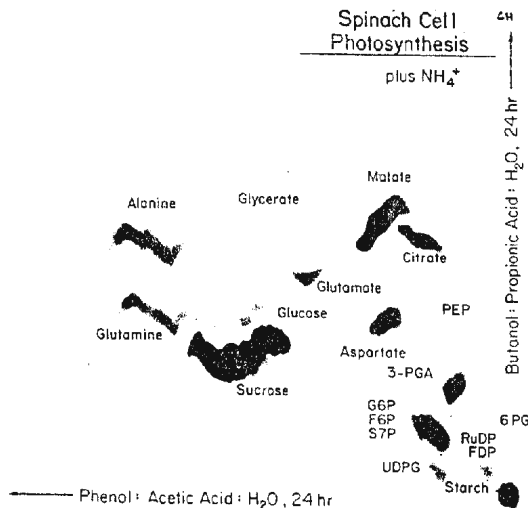

Fig. 4 *Two dimensional chromatogram of photosynthesis products of spinach cells (using labeled ^{14}C).*

mechanism. This has resulted in the development and optimization of new separation methodologies.

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Radiotracers and its Applications in Biology

Dr. A.G.C. Nair *joined Radiochemistry Division of BARC in 1969. Since then he is actively engaged in the development of radiochemical separation procedures of fission products and trace element determination using conventional, k_0, and prompt gamma-ray neutron activation analysis. He obtained his Ph.D. Degree from Bombay University in 1989 and has about 100 publications to his credit.*

Radio tracers have been in use in diverse fields of research and applications. It is George Hevesy who introduced and pioneered the concept of radiotracer for many applications in different fields like medicine, bilogy and mineral analysis. Its applications in biological sciences both to the study of the different biological functioning and has gained lot of importance comparable with the technical advances made. Applications of radiotracers in chemical research cover the study of reaction mechanism, kinetics, exchange process and analytical applications such as radiometric titrations, solubility product determinations and isotope dilution. In industry they are used for radiography with sealed sources, sterilization of medical products, process control in production technology, sewage sludge treatment, polymerization etc. They have been widely used in radio pharmaceuticals for various diagnosis and therapeutical purposes. In agriculture tracers are used as a radiation source for radiation induced mutations for producing better yielding seed variety and to study the uptake behaviour of nutrient elements in plants and fertilizer applications. This article deals with the salient features of radio tracers and a brief account of the labeled compound preparation and some of its applications in biology.

Radio tracer is a radio active isotope of an element whose behaviour is identical to that of the stable isotope of the same element. Radiation detection being very sensitive, the tracking of the stable element in a dynamic system by tagging with a tracer is highly sensitive. In most of the cases, radio tracers are the neutron activation products of the stable element. Application of radiotracers offers simplicity and are inexpensive. The main advantage of using a tracer is that it does not affect the system under study as the amount of the tracer is negligible compared to the stable element. In exceptional cases difficulties may arise directly or in directly when such physical constants like rate of reaction or chemical equilibrium are involved. The difference in behaviour between different isotopes of the same element is due to the difference in masses of the tracer and stable isotope. This mass difference will affect the kinetic energy of the molecules or will change the vibrational and rotational properties of molecules. This effect is termed as the isotope effect. The effect may become significant only for elements of low atomic weight ≤ 25. The case of hydrogen (^1H, ^2D, ^3T) represents an extreme case where differences in masses is high. They may not be expected to act chemically same, but can be put into useful advantage in tracing the functionality of several compounds of H particularly in a reaction. Similar is the case with ^{14}C and the stable ^{12}C.

Selection of a radiotracer depends upon several factors. One such criterion in the selection of a radio tracer is that the radioactivity associated with the tracer does not change the chemical and physical properties of the experimental system, i.e. the radiation effect is minimum. By minimizing the total radioactivity taken for the experiment the above effect as well the health and safety aspect are taken care of. Through the decay product of the radio-tracer, an entirely different element comes into

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picture. Another criterion is the total concentration that has to be kept at normal or optimum level by manipulating the specific activity of the radio tracer. In many cases the low concentration level of the tracers may lead to losses due to adsorption on the vessel or container since the surface area available for adsorption is very high compared to the concentration. The effect can be prevented by addition of non radioactive element (the stable element) known as carrier which can effectively fill all the adsorption sites. Another aspect to be taken into account is the complete isotopic exchange. This essentially means that the stable atom and the radio isotope must be in the same redox state. By following a redox cycle the radiotracer and the corresponding element can be taken to the same chemical state. Additionally, selection of a radiotracer is influenced by its availability, its half life and type of radiation it emits. The half life of the radio tracer should be long enough to avoid large correction due to the decay during experimental study.

Labeling the radio tracer to a specific compound is an important aspect of radio tracer applications. One of the primary tasks to study the tracing especially the functioning of biological phenomenon is to label the radio tracer with an appropriate compound. Labeling is carried out in a variety of compounds by standard synthesis procedure of organic chemistry. For ^{14}C labeling $Ba^{14}CO_3$ is the starting material and is often converted to CO_2 for synthesis. At present numerous labeled compounds are available commercially and can be used directly. Biosynthesis is another way to prepare labeled compounds. Living organisms or active enzyme preparations offer means of synthesizing certain labeled compounds. Certain proteins, vitamins, amino acids, sugars etc. can be produced by this route. ^{14}C labeled starch and sugars can be isolated from green leaves that have been exposed to $^{14}CO_2$. Another frequently used radio tracer in biology is tritium. Tritium labeling can be carried out by reduction with carrier free tritium gas or tritiated metal hydrides on a suitable precursor compound. Labeled compounds can also be prepared by exchange reaction with the compound with or without catalyst or by gas exposure where by the compound is mixed with tritium with carrier free

gas. The method is known as Wilzbach gas exposure method.

It is important to know the routinely used nomenclature while referring to a labeled compound. The position of a single labeled atom in a molecule is shown following the chemical name of the compound. Thus acetic acid 1-^{14}C is $CH_3{}^{14}COOH$ while acetic acid -2-^{14}C is $^{14}CH_3$—COOH. Chemicals are specifically labeled when all the labeled positions are included in the name of the compound. The labeled atom can also be uniformly labeled. For example L-Valine-14(U) implies that all the C atoms are labeled with equal amounts of ^{14}C. For Nominally(N) labeled compounds the designation only implies that only some part of the label is at a specific position and Generally labeled (G) depicts that there is a random distribution of labeled atoms in the molecule.

Tracing the chemical or physical process is one of the important tasks expected out of the radio tracer. In tracing a physical process the chemical identity of the tracer is not very important, like the evaluation of the process of mixing or in the determination of an inaccessible volume of a container and leak testing. Most of these are produced by (n,γ), or (n,p) or (n,α) reactions in a reactor, charge particle induced reactions, and fission product nuclei by separation from irradiated uranium. Since most of the biologically important substances are of origin the major part the studies are carried out by ^{14}C and ^{3}H. Some of the studies carried out by these radioactive tracers are: determination of age of biological materials, biodistribution of biomolecules, bioavailability of drugs, metabolic path ways and transport of molecules, biosynthesis of biomolecules in living organisms, velocity of enzyme reactions both invivo and invitro systems. Isotope dilution analysis also uses several radio tracers for analysis of the organic /inorganic constituents. The method is based on the changes in specific activity of a substance upon incorporation into a system containing an unknown amount of that substance. The technique consists of adding to the sample containing x g of the species, y g of a radioisotope form of the species of initial activity S_1 with counts/m/mg. After mixing, a small amount of the species is isolated from the mixture and its specific activity S_f is determined. The value of S_f

would be less than S_1. With this two measurements the unknown amount x is calculated on the principle of activity balance. Bioditribution study is based on the principle of Isotope Dilution. The water content and bio distribution of important compounds in living organisms such as plant and animals can easily be established by this method with out disturbing the physical and chemical equilibria. A known specific radiotracer is introduced and after optimum time period the compound of interest is withdrawn. From the specific activity decrease the total concentration of the compound can be arrived at. ^{131}I labeled plasma protein is used for estimating the total plasma protein and its distribution. In the analysis of aspartic acid in protein hydrolysate a labeled aspartic acid with known specific activity is added to the hydrolysate. After thorough mixing , aspartic acid is isolated in a pure form and its specific activity determined. From the decrease in the specific activity the concentration of aspartic acid is determined. In study of biosynthesis and transport studies one of the acclaimed examples is the photosynthesis occurring in plants which has been carried out by $^{14}CO_2$. Plant is exposed to $^{14}CO_2$ for different times and the ^{14}C is tracked upto the final stage of labeled glucose. ^{11}C labeled glucose has been extensively used for the study of brain metabolism. ^{15}O labeled CO, CO_2 H_2O are used for blood flow and volume determination. ^{18}F labeled ^{18}F-Deoxy-2 fluro-D-glucose (FDG) when administered into tissue , the FDG is converted to Fluro glucose-6- phosphate which can not be metabolized further and is trapped in tissue. This trapped tracer is used for imaging.

Specific destruction of the diseased cell, is very important in cancer therapy. Here radiotracers can physically or chemically be implanted to achieve specific destruction of the diseased cell. In this connection the application of ^{131}I in the treatment of thyroid is well known. Development of mono clonal antibodies that seek out particular cancerous cell and burn them is an emerging field. Radio labeled antibodies with tracers of ^{211}At, ^{131}I, ^{186,188}Re, ^{125}I, ^{90}Y can deliver dose at the required site without damaging to normal tissue. Another approach to the same problem is Boron Capture Therapy where the boron is located in the diseased tissue and subjected to neutron irradiation. The $^{10}B(n,\alpha)$ reaction releases the energy for destroying the affected tissue.

The largest number of applications of radio tracers are in biology and medicine. The main technical approach to solve the problem is based on auto radiography and radio-immino assay. Auto radiography is the oldest method of detecting radioactivity. In this method a radioactive sample is placed on a photographic emulsion and is used to locate a radionuclide in a tissue. In order to gain optimum spatial resolution in the image, an optical or electron microscope is used. Radioimmunoassay (RIA) is a highly sensitive method of determining the concentration of harmones, drugs, vitamins, enzymes, antigen serum proteins etc. in biological samples. It is based on the immunological reaction of antibodies and antigens. Details of RIA are described in another article in this issue.

The most rapidly expanding area of tracer application is in nuclear medicine. It deals with the use of radiation and radioactivity to diagnose and treat diseases. Radiopharmaceuticals are radiotracers used for diagnosis and therapy of various diseases. They can be classified into in-vivo and invitro radiopharmaceuticals. Invivo pharmaceuticals are administered into patients for diagnosis The diagnostic application etc invivo include scintigraphy of organs both static and dynamic imaging. Invitro application of radiopharmaceuticals include the well known radioimmunoassay technique. The radiotracers used in radiopharmaceuticals are ^{51}Cr, $^{57}/^{58}$Co, ^{59}Fe, ^{67}Ga, ^{81}Kr, ^{82}Rb, ^{99m}Tc, ^{111}In, ^{123,125,131}I, ^{133}Xe, ^{169}Yb, ^{195m,198}Au, ^{201}Tl . The radioisotopes used for therapy are particle emitters such as ^{32}P, ^{89}Sr, ^{90}Y, ^{131}I, ^{153}Sm, $^{186/188}$Re and ^{198}Au. The diagnostic use of radio tracers is for imaging of specific organs, bones, or tissue. Typical amount of radioactivity ranges from 1-30 mCi and 100-200 keV enegy radiation is preferred. Computerised tomography (CT) is used for improving the image where the photographic plate is replaced by one or more detectors and moving the imaging radiation with respect to the patient followed by software to process online image from the observed changes in counting rates. ^{11}C, ^{14}C, ^{13}N, ^{15}O, ^{18}F, ^{35}S and ^{47}Ca are some of diagnostic radio nuclides used in PET scans. Tomography can involve images generated by the transmission of radiation through the body or by incorporating radio tracers into the body and detecting the emitted radiation. The positron

emitting nuclide like $^{11}C,^{13}N,^{15}O$ and ^{18}F are introduced into the a region to be studied and the two 0.511 MeV annihilation photoes emerging in opposite direction are measured in coincidence by an array of detectors to costruct latter a 3D image of the area where the decay ocuured. These radiotracers are short lived and are mainly produced by proton irradiation of the appropriate stable element in a cyclotron. $^{14}N(p,\infty)^{11}C$, $^{18}O(p,n)^{18}F$. ^{99}Tc, $^{201}Tl,^{67}Ga,^{111}In,^{125}I$ are all single photon emitters and are used to determine the presence and distribution of the radionuclide. Multiple images are taken over a short time to study the dynamic behaviour of the system. Though presently enzyme and fluorescent molecules have replaced radioisotopes in few cases, the simplicity and sensitivity achievable by radiotracers in the study of biology will continue and radiolabeled compounds will remain as a unique and simple tool in biology and bioscience.

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Radioimmunoassay : Expanding Horizons from Clinical to Non-Clinical Applications

Dr Grace Samuel joined the Radiopharmaceuticals Division in 1976 and is one of the early researchers in radioimmunoassay. She has been instrumental in the development of RIA procedures of small molecules such as steroids and drugs. Since past eight years, she is carrying out research on the development of in-vivo radiopharmaceuticals. She is presently the Co-ordinator for the training course on "Radioimmunoasay and its clinical applications" conducted by Bhabha Atomic Research Centre. Dr Grace Samuel has served as an IAEA expert in the field of radioimmunoassay and has over 40 publications in International journals.

Dr. M.R.A. Pillai is presently the Head, Radiopharmaceuticals Division, BARC and concurrently holds the position of Senior General Manager, Medical and Biological Products Programme (MBPP), Board of Radiation and Isotope Technology (BRIT). After graduating from the BARC Training School in 1976, he obtained his M.Sc. and Ph.D. degree from the Bombay University. He worked as a visiting professor at the University of Missouri-Columbia, USA and was a technical co-operation expert of IAEA in several countries. He is a recognized guide for M.Sc. and Ph.D. degrees of the Mumbai University. He has co-authored a book, chapters in several books and has about 120 publications in international journals. He is one of the past editors of the IANCAS and currently the Secretary of the Society of Nuclear Medicine, India.

"Human Body is a conglomeration of chemical reactions,
when they are deranged only chemical medicine can help"

Paracelsus

Introduction

The knowledge that the human body and its functions are controlled by well programmed biochemical reactions was known for a long time as exemplified by the writing of Paracelsus, the alchemical genius of the middle ages and the precursor of modern day chemical pharmacology and therapeutics. The above knowledge also brought out the necessity to develop biochemical assays for estimating them in body fluids. The sensitivity and specificity of the physico-chemical analytical techniques available in a clinical pathology laboratory in the early part of the twentieth century were sufficient for the quantitative estimation of a large number of bio-molecules and metabolites present in serum. The biomolecules thus measured included glucose, albumin, creatinin, iron, immunoglobulins etc. However, the discovery of the hormones starting with 'secretin' in the year 1902 by Bayliss and Starling added a new dimension to the biochemistry of the human body. The discovery of several more hormones secreted by other endocrine glands such as the pituitary, thyroid, adrenals, gonads and pancreas as well as the understanding of their effects on perfecting the balance of various body functions such as metabolism, growth and reproduction slowly lead to the emergence of a completely new field called endocrinology. The endocrine glands, their secretions, the mechanism of

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their action and the structure of several hormone molecules were known by the middle of the twentieth century. However, the sensitivity barrier of the analytical techniques available at that time posed a major problem, in that none of these hormones could be estimated in human serum so that their levels could be used as a diagnostic tool. Thus the field of endocrinology remained as more an art than science and the diagnosis were made by clinical examination relying more on the experience and imagination of the practising physicians. The blood level of some of the biomolecules as compared to a few important hormones are given in Table 1.

Table 1 - Concentration of a few clinically important substances in blood

| Concentration	Substance
10 mmol/L	Glucose
1	Albumin
100 μmol/L	Creatinin
10	Iron
1	Immunoglobulin
100 nmol/L	Thyroxine, Cortisol
10	Progesterone, Testosterone
1	Estradiol
100 pmol/L	Insulin
10	Free T3

Radioimmunoassay

In the fifties, Dr. Rosalyn Yalow a Ph.D in nuclear physics and Dr. Solomon Berson, a medical doctor were interested in studying the in vivo metabolism of insulin, a hormone secreted by the pancreas gland which was identified to be responsible for the metabolism of glucose, the energy source of the living cell. It was Yalow's idea that insulin labeled with ^{131}I could be used for this purpose. They expected a faster metabolism of insulin in diabetic patients as compared to normals. However, to their surprise, the results were otherwise. They observed that diabetic patients who were receiving insulin injections showed higher retention of the labeled insulin. Through a very careful and meticulous in vitro analysis of the blood collected from these patients, they found that in insulin treated diabetic patients, the labeled insulin

was bound to a macromolecule and hence retained longer in the body. The macromolecule binding the labeled insulin was later identified by them to be the insulin specific antibody. Yalow and Berson developed a method for the estimation of insulin by using the same antibody and the radioisotopically labeled insulin as a tracer molecule. As this assay technique used radioactivity as well as antibody, they named it 'Radioimmunoasay' (RIA). Millions of needy patients the world over have derived the benefit from this assay technique for better diagnosis and management of endocrine disorders, infectious diseases and a wide variety of cancers.

Principle of Radioimmunoassay

Two important criteria in all the analytical techniques are: (a) an excess of reagent is used and (b) the product formed is measured. RIA differs markedly in that both the above criteria are violated. RIA is a 'limited reagent' assay. The reagent, antibody, is used in much lower concentration than that of the analyte. The assay is based on a competitive reaction as depicted below.

$$\begin{array}{ccc} Ag^* & & Ag^*Ab \\ & + Ab \Leftrightarrow & \\ Ag & & AgAb \end{array}$$
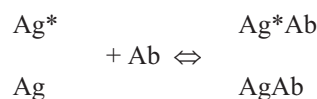
where Ag is the analyte or antigen to be measured, Ab is the antibody which is the reagent in the assay and Ag* is the ^{125}I-labeled analyte which mimics Ag in all respects except that it has a radioactive iodine atom tagged to it. The analyte or antigen (Ag) and a radioactively labeled antigen (Ag*) compete for a limited but fixed amount of antibody. Both Ag* and Ab are taken in fixed and limited concentration and the concentration of Ag is varied. It can be visualized that, in the absence of Ag, all the Ab will be used up by the Ag* to form the complex Ag*Ab. As the concentration of Ag is increased, a part of the antibody will be used by the Ag to form the complex AgAb and correspondingly the Ag*Ab concentration will decrease. Thus the amount of Ag*Ab formed and hence the amount of radioactivity associated with the complex is inversely related to the concentration of Ag. By using known amount of Ag as standards, a standard curve can be set up. The concentration of an unknown sample can be measured from this standard curve (Fig.1).
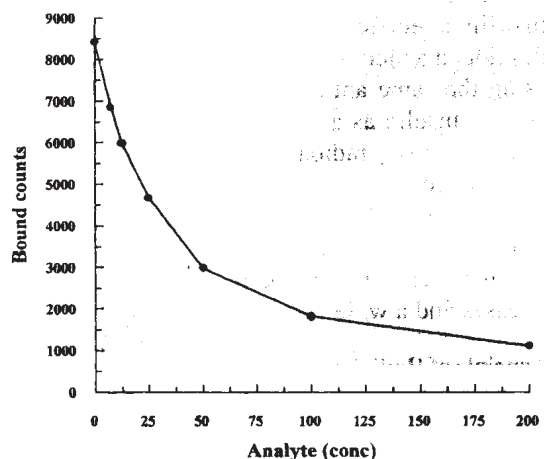
Fig. 1   A Radioimmunoassay standard curve

Advantages of RIA

Its remarkable sensitivity makes it possible to use extremely small quantity (<0.01 mL) of the serum sample. The high specificity of the assay rendered by the use of antibody avoids the need for any sample preparation (clean-up procedure) or extraction of the analyte prior to its estimation. The samples can be sent from remote places to RIA laboratories in the cities for analysis and hence patient movement is not necessary.Apart from high sensitivity and specificity, reproducibility, rapidity, simplicity and low cost are other advantages of radioimmunoassay.

Requirements for a radioimmunoassay

The essential prerequisites for a radioimmunoassay are (i) specific and avid antibody (Ab, the reagent), (ii) a radiolabeled antigen (Ag*), (iii) cold antigen (Ag) of known concentrations (standards) and (iv) a separation system to separate the antigen-antibody complex from the free antigen.

Antibody

The quality of antibody, the key reagent in radioimmunoassay, will significantly contribute towards the specificity and sensitivity of the assay. Antibodies, which are largely immunoglobulins, of molecular weight 150,000 daltons, are prepared by immunising laboratory animals such as rabbits, guinea pigs, goats and sheep with the antigen that is emulsified with an adjuvant. The emulsification of the antigen gives a better and longer exposure of the antigen in the animal system, thereby stimulating the immune system of the animal to elicit the production of antibodies. The primary injection is followed by secondary injections or booster doses at regular intervals of three to four weeks. The blood of the immunized rabbit collected during 10-20 days after third or fourth booster dose generally yields antibodies of good quality. The sera is separated from the blood and characterized for its titre (the concentration), avidity (energy of reaction) and specificity in relation to structurally similar molecules. The antibodies produced in this manner are referred to as polyclonal antibodies. The polyclonal antibodies are a heterogeneous population of antibody. Monoclonal antibodies are also finding large scale applications in immunoassays. Monoclonal antibodies as the name suggests is a homogenous population of antibodies and are produced from a single clone by a technique called 'hybridoma'. In this technique, a B-lymphocyte (spleen cells) from an immunized animal is fused with a myeloma cell of mouse origin to form a hybridoma cell. The hybridoma cell acquires the property of producing antibody from the B-lymphocyte and the infinite life from the myeloma cell. The hybridoma cells are allowed to grow in a selective hypoxanthine- aminopterin-thymidine (HAT) medium. After limiting dilution and screening for antibodies, the selected clones are preserved and the antibodies are harvested as and when desired. With this method, antibodies could be made available in pure form and in significant (mg) quantities.

Radiotracer

The isotope of choice for use in radioimmunoassay is ^{125}I owing to its long half life (60 days), low gamma and X ray energy (28 & 32 keV), high counting efficiency, absence of particulate emission, 100% isotopic abundance, and ease of incorporation of the iodine atom into the tyrosyl residue available in most of the antigens. The

incorporation of the iodine atom is achieved by using a mild oxidizing agent which helps in the electrophilic substitution of it into the tyrosyl atom, present in most of the protein hormones. Absence of tyrosyl or other iodinatable residue in an antigen necessitates the need for modification of the substrate such as steroids and drugs to introduce tyrosyl or histamine moieties. The radioiodinated compound is purified by gel filtration, thin layer chromatography (TLC) or high pressure liquid chromatography (HPLC). The radiolabeled reagent enables the physico-chemical reactions to be monitored even when exceedingly small number of molecules is involved. Moreover, contaminating radioactivity deriving from extraneous sources is not normally present in biological fluids thus avoiding any background interference.

Standards

In RIA, since the response of the unknown is compared to that of a set of standards of known concentration, it is essential that the standards should be identical to the analyte being assayed. The potency of the standards are compared with reference preparations from agencies such as World Health Organisation (WHO) or National Institute of Health (NIH).

Separation System

A separation of the bound complex from free is essential at the end of the reaction. The difference in the physico-chemical properties is exploited in selecting a reagent to separate the two phases. Dextran coated charcoal, second antibody, polyethylene glycol, were some of the earlier methods used. The second antibody along with PEG, commonly known as the combination technique is a more efficient and rapid method. Presently, solid phase assays with antibody coated on tubes or on magnetic cellulose have become more popular due to its simplicity and user-friendliness.

Immunoradiometric Assays (IRMA)

Miles and Hales in the year 1968, put forward a modification of radioimmunoassay, later known as the Immunoradiometric assay (IRMA). The new method suggested the use of excess reagent as in all conventional assays and unlike that used in radioimmunoassay, which is a limited reagent method. In this analytical technique, the sensitivity available from the high energy antigen-antibody reaction is fully exploited due to the use of excess reagent since all the analyte is converted to the product.

In IRMA, an excess amount of labeled antibody (Ab*) is allowed to react with the analyte (Ag) either from the sample or standard.

$$Ag + Ab^* \rightarrow AgAb^* + Ab^*$$

The amount of AgAb* formed is in direct proportion to the concentration of the analyte. Antigen-bound antibody fraction is separated and assayed for radioactivity. The concentration of the unknown can be read from a standard curve (Fig. 2).

'Two site' IRMA

The immunoradiometric assay concept could not be fully realized due to the non-availability of pure antibody for radiolabeling and the absence of a suitable separation method as the conventional separation methods used in RIA could not be used in IRMA due to the small difference in the size of the bound and the free fraction. In the year 1976, Kohler and Milstein, invented the hybridoma technique for the production of monoclonal antibodies. With the availability of antibody in pure form which was suitable for radiolabeling and the development of two site IRMA' technique by Addison and Hales which facilitated the separation of the bound and free fraction, this new technique took a rapid pace. 'Two site IRMA' relies on the immunoextraction of the analyte by a solid phase antibody and subsequent reaction of the solid phase bound complex with the radiolabeled antibody. An excess amount of antibody is coated on a solid phase such as polystyrene or polypropylene tubes. This solid phase antibody binds to a site on the standard analyte or sample analyte to form a complex (Fig. 3). This is followed by the addition of radiolabeled antibody. The radiolabeled antibody binds to a second site on the antigen, forming AbAgAb* complex on the solid phase, effectively sandwiching the antigen (Ag) between the solid phase and labeled antibody.

The use of excess reagent makes IRMA more sensitive than RIA. The use of two antibodies in a 'two site IRMA' also makes it more specific than
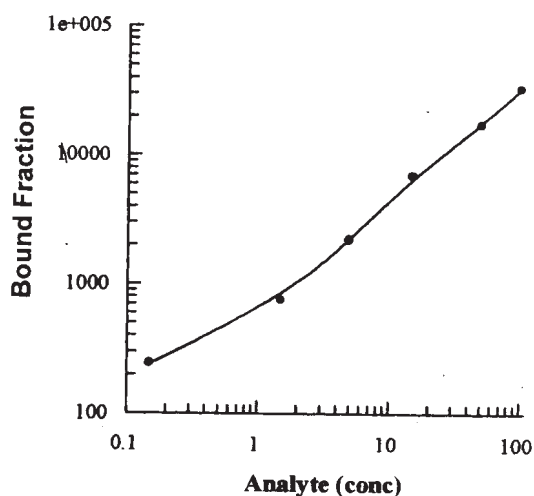
Fig 2   An immunoradiometric assay standard curve

Fig. 3   Illustration of the Principle of "Two Site IRMA"

RIA. Being excess reagent assays, IRMA is more robust and requires shorter incubation period.

Non-isotopic immunoassays

In RIA and IRMA, the endpoint signal is measured as the radioactivity associated with the antigen-antibody complex. Any marker whose activity could be measured at the end of the reaction could also be used to label the antigen or antibody to develop immunoassays based on limited or excess reagent. A few of these labels, which are used as an alternative to radionuclides are enzymes, chemical luminescent compounds, fluorophores, bioluminescent markers, various particulates, metal atoms, bacteriophages etc. Of the above, enzyme, chemiluminescent and fluorescent markers are now widely used.

In enzyme immunoassay, the enzymatic activity emanating from the labeled antigen or antibody is measured as the end point signal. At the end of the assay, the enzyme associated with the antigen-antibody complex is allowed to react with a suitable substrate to give a colored product, the intensity of which, is measured by a spectrophotometer.
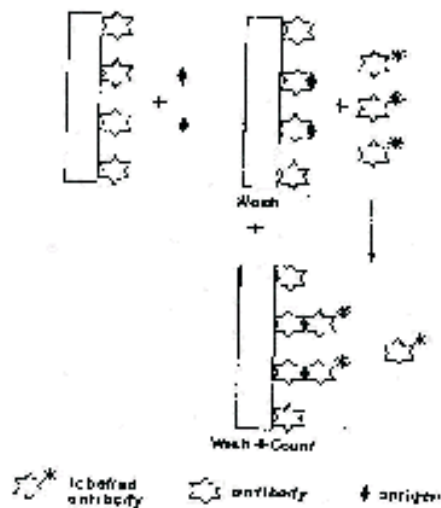
Chemical luminescent substances are compounds that give out light during a chemical reaction. The label associated with the complex at the end of the incubation is reacted with an oxidizing agent such as peroxide and the light given out is measured by a photometer. Luminol and its derivatives are commonly used as markers in chemiluminescent immunoassays.

Fluorescent substrates such as fluorescein are molecules that fluoresce on appropriate radiant excitation. In fluoroimmunoassay, at the end of the reaction, the end point signal is measured by the light given out upon excitation of the fluorescent molecules by an external source. A modification of this assay, known as time-resolved fluoroimmunoassay, where the light is measured after the background fluorescence has decayed, makes use of europium chelates as labels which has a longer decay time. Time resolved fluoroimmunoassays have much lower interference from the matrix. Assays using fluorescent markers give much higher sensitivity than provided by the isotopic assays.

Ready-to-use kits

Currently ready to use immunoassay kits for a wide variety of substances are available from

various suppliers in various sizes. All the reagents required to carry out the assay are formulated in the form of a kit. Most of the kits include quality control samples to monitor the performance of each assay.

Clinical Applications of Immunoassays

Radioimmunoassays have been developed for the measurement of several hormones, vitamins, drugs, viruses, enzymes etc. present in human body. The commercial introduction of ready-to-use kits enabled many hospitals to perform radioimmunoassay, subject to the availability of a simple radioactive counter. Major advances in the diagnosis and treatment of the body's major hormone systems, including thyroid function, growth and fertility were achieved with the introduction of RIA.

Endocrinology

The most important application of RIA is in the management of thyroid disorders. Estimation of the thyroid hormones, triiodothyronine (T_3), thyroxine (T_4) and thyroid stimulating hormone (TSH) is used for the diagnosis of thyroid disorders. Thyroid disorders include hypothyroidism, such as cretinism and myxodema, and hyperthyroidism such as thyrotoxicosis and Grave's disease. In neonates, symptoms of hypothyroidism are clinically undetectable until three months of age, which may by then lead to brain damage. RIA of thyroxine (T_4) levels or thyroid stimulating hormone (TSH) in the blood of newborn infants is used as a screening test in many hospitals on a routine basis to diagnose neonatal hypothyroidism in time to prevent irreversible brain damage. Levels of TSH, before and after thyrotropin releasing hormone (TRH) stimulation, a pituitary hormone, help in the differential diagnosis of primary, secondary and tertiary hypothyroidism.

Using RIA of insulin, physicians could distinguish between the diabetics who lose the ability to make insulin during childhood and those who produce insulin but during adulthood lose the ability to use it. This helped in deciding a better line of treatment of diabetes.

Estimation of growth hormone, which is essential for bone development and growth, helped in the early diagnosis of dwarfism in children. RIA

of growth hormone is also useful to find out whether abnormal bone growth is caused by over secretion of growth hormone.

Estimation of human chorionic gonadotrophin (hCG) is useful for the detection of pregnancy, monitoring its progress, to establish the gestational age as well as for proper management of patients with complicated pregnancies such as ectopic pregnancy, threatened abortion and foetal distress. RIA of luteinizing hormone (LH) and follicle stimulating hormone (FSH) is used for identifying the causes of infertility and better understanding of the problems associated with child bearing and infertility. Estradiol determinations have proved to be of great value in many disorders such as investigations of precocious puberty in girls, differential diagnosis of amenorrhea, monitoring ovulation induction and functioning of ovaries. Levels of testosterone are useful in detecting hypogonadism, testicular tumors in males and diagnosis of hirsutism in females. Prolactin levels are extremely useful for identifying pituitary adenomas and cortisol levels are useful in diagnosing Cushings' syndrome and Addison's disease.

Pharmacology

RIA of drugs has gained importance owing to the increasing concern for the safety and toxicity of the drugs. It has been clearly established that use of clinical pharmacokinetics to predict drug concentrations and to optimize dosages results in better and more cost effective healthcare through individualizing a patient's therapeutic regimen. It is important to monitor plasma levels of drugs having narrow therapeutic window (therapeutic drug monitoring, TDM). Drugs such as phenytoin, theophylline, cyclosporin, morphine, gentamycin and antidepressants are estimated by RIA. In pharmacology, the assays are used for estimation of bio-evaluation of drug formulations. From heroin in drug abusers to steroids in athletes and antibiotics in patients, RIA can estimate the concentration of drugs in blood, urine and saliva. In forensic sciences, RIA is used for investigating deaths due to intentional overdosing of drugs.

Infectious Diseases

RIA is used for detection of bacterial and viral antigens such as hepatitis-B surface antigen. It is also used for screening donors blood for hepatitis-B antigen as well as other infectious diseases. Most of the early diagnostic kits for AIDS were based on immunoassay technology.

Tumor Markers

RIA of tumor markers such as alphafeto-protein (AFP), carcino-embrionic antigen (CEA), β-hCG for chorio-carcinoma, prostate specific antigen (PSA) for prostate cancer are available for detection and management of cancer. They serve as valuable tools for follow-up of treatment and detection of any recurrence.

Non-Clinical Applications of Immunoassays

Immunoassays are extremely versatile techniques and have played a leading role in clinical applications. Recently there has been an increasing interest in the use of this technique in non-clinical applications such as veterinary science, food processing industry, drug industry, forensic science and environmental monitoring.

Veterinary Science

Veterinary science is one of the early beneficiaries of the immunoassay technique. The presence of residual antibiotics in animal foods could lead to development of drug resistant microorganism that may pose harmful effects to humans. Hormones and related compounds are used to increase animal growth. But some of these agents are potential carcinogens to humans and hence it was necessary to monitor the antibiotic residues and hormones in animal tissues. An assay for anabolic steroids in food products could be used for estimating contamination in meat and meat products. Progesterone in milk is a very good indicator for identifying luteal phase defects in cattle and to detect missed conception. It provides information both on problems in breeding management and livestock improvement as well as in artificial insemination services.

Food Industry

In food industry, immunoassays contribute tremendously to the quality and safety of food supply. It helps to manipulate the production and processing by knowing the level of flavor constituents such as limonin in grape fruit and hespiridine (flavanone) in orange. RIA has been used to identify food sources rich in pantothenic acid and bioavailability of folates in plants. It has also been used to detect indole acetic acid in nanogram quantities in a variety of food crops such as maize, broad bean, pea and sunflower. Immunoassays have been explored extensively for application in detecting and estimating food additives and contaminants that render food unsafe.

Estimation of mycotoxins by immunoassay is another significant development. Mycotoxins are low molecular weight compounds produced by a group of fungi. They can produce acute and chronic effects on human and animal health. Aflatoxins are mycotoxins that are primarily produced by the strains of Asperigillus parasiticus. Aflatoxins are toxic secondary metabolites and are carcinogenic. Aflatoxin B1 is the most potential carcinogen and is generally found in peanut, corn and cottonseed. The contamination of aflatoxin in agricultural commodities has been the subject of serious concern at national and international levels. Regulations governing aflatoxin levels in food and feed are becoming stringent all over the world. In India, as per the Food Adulteration Act, 1954, presence of aflatoxin should not exceed 30 ppb. The levels are still lower in other countries. Hence, agricultural commodities from India face rejection due to higher aflatoxin levels. At present, immunoassay due to its specificity and sensitivity are being used to measure the aflatoxin contamination in food and food products. Current management of aflatoxin contamination begins in the field, continues throughout harvest, drying and storage and culminates with the manufacturing process.

Drug Research

In pharmacognosy, immunoassays are used for the analysis of specific chemical constituents in plant tissues and are now used to detect and quantitate a wide range of plant constituents of pharmaceutical importance.

Forensic Investigations

Radioimmunoassay has been used for screening post-mortem blood for drug abuse such as opiates, amphetamines, cocain and barbiturates. Hair analysis for drugs of abuse provides long-term information on an individual's drug use.

Environmental Science

Environmental contamination is a worldwide problem. Application of pesticides that are used in agriculture, horticulture and forestry as conservatives against microbial infestation is partly responsible for this environmental contamination. Immunoassays are now used for the estimation of antibiotic, toxic alkaloids, pesticide, herbicide, fungicide, detergent and other potentially toxic residues in piped water and well water, soil and vegetation. The need for rapid and simple tests that can be performed on site without requiring sample transfer to the analytical laboratory has been the driving force for the development of field portable immunoassays.

Immunoassay of Metals

Heavy metals are of particular concern to both the general public as well as the regulatory agencies because of their persistence in the environment and their ability to be mobilized by weather changes and hydrology. Experimental and epidemiological studies are providing substantial evidence that low-level chronic exposure to heavy metals such as Cd and Hg can contribute to an increased risk of cancer. Thus the ability to rapidly and inexpensively monitor trace metals has become a necessity. Even with the best analytical methods, problems arise when it is scaled to handle a large number of samples. These problems motivated the search for low-cost, rapid automated systems. Immunoassays satisfies these criteria availability of immunoassays for specific metal ions will lower analysis costs and provide a useful adjunct to more traditional methods of metal analysis.

The immunoassay technique is theoretically applicable to any substance for which a specific antibody can be generated. Developing a metal specific antibody was a challenge to the immunoassayists. This was achieved by using bifunctional derivatives of metal ion chelators (EDTA, DTPA, DOTA) covalently conjugated to proteins and loaded with the desired metal ion. These conjugates were used to prepare hybridoma cell lines that synthesized metal-specific monoclonal antibodies.

Conclusion

"The first telescope opened the heavens; the first microscope opened the world of microbes; radioisotopic methodology, as exemplified by RIA, has shown the potential for opening new vistas in science and medicine" (Rosalyn Yalow, Nobel Lecture, 1977). Yalow and Berson innovated the radiotracer technique of George Hevesy by using a specific biomolecule, the antibody, as the reagent to invent a highly specific and sensitive assay technique the application of which has outlived the expectation of the inventors. The beneficiaries of the RIA technique far outnumber that from all other radioanalytical techniques put together there by making RIA as one of the epoch making scientific discoveries of the twentieth century.

Suggestions for further reading

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Gamma Ray Spectrometry

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Introduction

Gamma ray spectrometers are the most common equipment in any radiation monitoring laboratory. Whether one is engaged in measurement of radioactivity in environment, or measurement of elemental composition (major, minor or trace level) of samples by neutron activation analysis, or study of reaction mechanism of nuclear reaction/fission by radiochemical methods or carrying out research (using radiotracer) in any field, γ-ray spectrometry forms an integral part of the laboratory. In the early 1950's, the development of NaI (Tl) detector led to the modern era of γ ray spectrometry. However, the energy resolution of the NaI (Tl) detector (~ 7% for 661 keV of ^{137}Cs) required chemical separation of the eluent of interest. The advent of Germanium and Silicon detectors in the 1960's led to a revolution in the field of γ-ray spectrometry. These detectors have an energy resolution of (~ 0.1 - 0.2 %) and hence preclude the purification of the radionuclide. The γ-ray spectrometers based on Germanium coupled with the computer based multichannel analysers with good softward for spectral analysis have simplified the radiometric assay technique enormously. The present article gives a brief account of the basic interaction of γ-rays with matter followed by the principle of semiconductor detector based γ-ray spectrometry system and the peak shape analysis program.

Interaction of γ- rays with matter

Gamma rays interact with matter mainly by three mechanisms, namely, photoelectric absorption, Compton scattering and pair production. In photo electric absorption the γ-ray photon interacts an absorber atom in which the photon completely disappears and a photoelectron is produced from one of the bound shells of the absorber atom. The KE of the photoelectron (E_e) is given by

$$E_e = E\gamma - E_b \qquad (1)$$

Where, E_γ is the energy of incident photon and E_b is the binding energy of electron in the original shell. The vacancy created in the electron shell is quickly filled by electronic rearrangement associated with emission of X-rays or Auger electron. If these are also stopped in the absorbing medium, all the photon energy is deposited in the medium. The cross section for photoelectric absorption depends upon the atomic number (Z) of the absorber and energy of the photon (E_γ) as

$$\sigma_{PE} \propto \frac{24}{E_\gamma^3} \qquad (2)$$

In Compton scattering the photon collides with an loosely bound electron and is scattered transferring part of its energy to the struck electron. The energy of the scattered photon depends upon the

incident photon energy and the angel (θ) at which it is emitted.

The scattered photon may either escape or further undergo Compton Scattering or photoelectric absorption. Thus, Compton scattering may lead to incomplete deposition of photon energy and usually gives rise to Compton continuum in the γ-ray spectrum. The cross section for Compton scattering depends upon the Z of the absorber and E_γ of the photon as,

$$\sigma_{CS} \propto \frac{Z}{E_\gamma} \qquad (3)$$

For γ-rays having energy more than 1.02 MeV the energy of photon may be converted to a positron electron pair in the Coulomb field of the nucleus. The excess energy (E_γ – 1.02) is shared between the positron and electron as kinetic energy, which are slowed down in the stopping medium. The positron when moderated to thermal energy gets annihilated with an electron, giving rise to two photons of 511 keV each though one in 372 events three photons may also be emitted. The 511 keV photons are emitted at 180° with respect to each other. Depending upon the size of the absorber either both or one of them may escape the absorber leading to single or double escape peaks in the γ-ray spectrum or both might be absorbed resulting in full energy deposition. The cross section for pair production varies with Z of the absorber as

$$\sigma_{PP} \propto Z^2 \qquad (4)$$

and it increases with the energy of the photon.

Other interaction processes like Rayleigh Scattering from bound electron and Thompson Scattering from unbound electron are not important from the point of view of radiation detection and hence are not discussed here. When γ-rays pass through an absorber the intensity of the transmitted γ-rays decreases exponentially with the thickness of the absorber.

$$I = I_0 \, e^{-\mu x} \qquad (5)$$

Where μ is the linear attenuation coefficient.

$$\mu = \sigma \rho N_A / M \; (cm^{-1}) \qquad (6)$$

$$\sigma = \sigma_{PE} + \sigma_{CS} + \sigma_{PP} \qquad (7)$$

σ = Cross section, ρ = Density of the absorbing medium, N_A = Avogadro's number and M = Atomic Weight or Molecular Weight

γ-rays Sources

Gamma rays are emitted when excited nucleus deexcites to lower energy level. Excited states are populated subsequent to radioactive decay e.g. α, β decay and in nuclear reactions.

Experimental set up for γ-ray Spectrometry

Modern γ ray spectrometry systems are based on high purity germanium detectors (HPGe). In a single crystal of semi conducting material such as Ge, the sharply defined atomic electron states are broadened into bands of energy states that are characteristic of the crystal as a whole. In the absence of excitation, the outer electrons are bound in an energy band called valence band (VB). The next higher states lie in the conduction band (CB), which is separated from VB by an energy known as band gap.

The Ge detectors are operated in reverse biased mode. In the reverse biased diode, the electrons from the n side are attracted towards anode and the holes from p side are attracted towards cathode thus creating an intrinsic region with no charge carriers. This forms the active volume of the detector. The band gap between VB and CB for Ge is 0.67 eV. However the W value, that is, the energy required to produce one effective ion e^--h^+ pair is 2.96 eV as some of the electrons are trapped in the defects and impurity centers. The operation of the detector involves,

1. Conversion of the photon energy to kinetic energy of electron (and positrons) by PE absorption, Compton Scattering or pair production.

2. Production of e^- -h^+ pairs by these electrons.

3. Collection and measurement of these charge carriers at the respective electrodes.

A block diagram of the HPGe detector system is given in Fig. 1.

When a photon interacts in the crystal, bound electrons are excited to CB by the primary electron from the interaction. These primary electrons can create secondary electrons if sufficiently energetic. Through this cascading process, the energy of the primary e^- is expended in production of several e^--h^+ pairs that are free to be collected at the electrodes of the diode. Collection of this charge requires an electric field gradient of 1000 V /cm. The applied voltage or bias is chosen low enough to minimize the probability of breakdown, but high enough to provide good charge collection and having good peak shapes.

Semiconductor materials are either p type (rich in acceptor impurities) or n type (rich in donor impurities). In early days the noise level due to the presence of acceptor impurities would totally mask the pulses from the photon. To reduce this leakage current to an acceptance level, it was necessary to create an intrinsic region within the crystal, devoid of free charge carriers. This was done by drifting Li^+ ions in the germanium crystal. Lithium was deposited on the upper surface of the p type crystal and drifted through the larger part of its volume. Lithium is an interstitial donor and will compensate the acceptor impurity creating the intrinsic region. This is what is called a Lithium drifted Germanium or Ge(Li) detector. In such a detector lithium will continue to drift significantly at room temperature and hence the detector must be cooled to 77 K at all the time.

For sufficiently pure germanium, the desired intrinsic region can also be achieved directly without compensation by creation of a diode structure. This structure may be created by evaporating lithium on one surface of the p type Ge and allowing it to diffuse

into the Ge for a short time period and a short distance. A reverse bias applied to this n-p junction pushes the majority carriers from the junction on both sides, creating the intrinsic region. A detector made this way is called an intrinsic or high purity (HPGe) detector. In contrast to Ge(Li), HPGe detectors can be stored and transported at room temperature. In addition to the electrons that are excited to CB by photon interactions, electrons are excited thermally and this mode of excitation produces statistical noise background. To minimize this noise semiconductor photon detectors must be operated at reduced temperature (77 K).

HPGe detectors are available in two forms, p type or n type. In p type HPGe the n^+ layer prepared by lithium diffusion from one end acts as +ve electrode and the metal contact on the other side acts as a -ve electrode. In the coaxial detectors the p type Ge crystal is grown on a metal contact at the center and the outer surface is diffused with Li, the diffuse layer can be as thick as 600 µm and hence the p type Ge has lower efficiency for low energy X rays and γ rays. In the case of n type HPGe the Ge crystal is grown on a metal contact and the surface is doped with p type boron by implantation. Since the thickness of the p layer can be controlled to as thin as 0.3 µm, n type Ge detectors are sensitive to low energy photons. Thus the useful energy range in p type Ge is above 40 keV and in case of n type Ge photons down to 5 keV can be detected.

Electronics

Bias Voltage

In order to collect the electrons and holes formed in the detector, a bias voltage must be applied
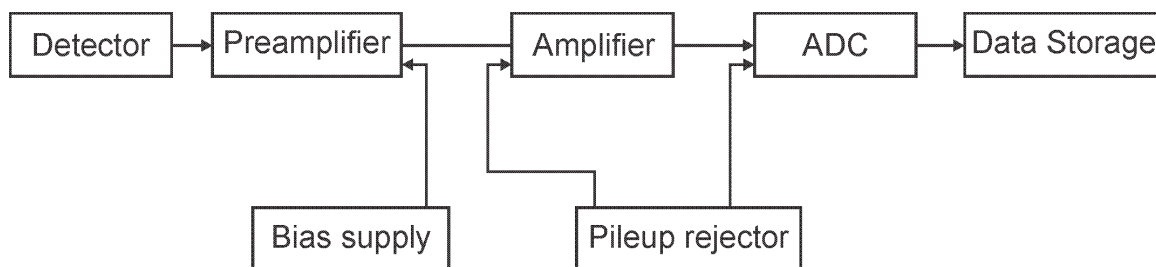

Fig. 1   Block diagram of a HPGe detector system

across the detector. The voltage is chosen low enough to avoid breakdown but high enough to have complete charge collection. Typical bias voltage is 3000 V and 4000 V but depends upon detector volume. Before connecting the bias supply to the detector the polarity of the voltage must be set correctly.

Preamplifiers

Modern semiconductor detectors use charge sensitive preamplifier, which is usually housed in the detector assembly in order to minimize the noise. The input stage of the preamplifier is usually a field effect transistor (FET), which is cooled in the same way as the detector. The preamplifier includes a feed back circuit which is generally achieved by resistive feed back. The height of the pulse from the preamp should be proportional to the charge collection in the detector and if all the photon energy was deposited in the detector it should be proportional to photon energy.

Amplifier

The preamplifier pulses are low height (typically 100 mV) and are amplified. The important characteristic of the amplifier are the linearity, output pulse shape, gain stability and the noise level. The shape of the output pulse is adjusted by changing the time constant which can vary from 2 to 10 μs. Best resolution is usually achieved with longer time constant but this increases the dead time and random summing. Most amplifiers provide both unipolar and bipolar output. Unipolar output gives better signal to noise ratio. In case there is a negative undershoot or positive overshoot in the unipolar output, the spectrum has or lower or higher energy tailing. This problem is solved by pole zero cancellation. Typical count rates which can be handled by commercial amplifiers are 2 kHz – 20 kHz. As the count rate increases, pile up effects and random summing spoil the resolution and result in incorrect data. Now a days gated integrated amplifiers are available which significantly enhance the operating count rate of the system.

Multichannel Analyser

The pulse height distribution of amplifier pulses is measured by means of an analog to digital converter (ADC), which converts the analog output information of the amplifier into digital quantity called channel. There are two types of ADCs in use- the Wilkinson type and the successive approximation type. In the Wilkinson type ADC, a clock is started simultaneously with a ramp voltage, which increases linearly with time. The clock is stopped when the ramp voltage becomes equal to the amplifier pulse and an event is recorded in the corresponding channel. In this type of ADC the time required to analyse a pulse increases with the pulse amplitude. Tyically for a 100 Mhz clock it takes about 40 μsec to analyse a pulse to go into channel 4000. In the successive approximation ADC the analysis time is independent of the pulse amplitude. Important characteristic of an ADC are the integral and differential linearity, zero stability and precision of live time clock, which is a part of ADC.

Pile up Rejection

When the count rate of the source is high, partial summing of two or more pulses leads to distortion in the peak shapes. This pile up of pulses can be eliminated by providing circuitry for pile up rejection in the amplifier. Usually one can measure the time spacing between the pulses in a fast channel without worrying about the pulse amplitude. The slow channel pulse, which is determined to be closely spaced in time can be rejected by turning off the ADC at the time they would reach it.

Spectrum Stabilization

Due to the variation in temperature and electronic drift, the gain of amplifier may change particularly when counting is continued for long period of time. Modern MCA Cards have the option to adjust the zero and the gain of the ADC so as to maintain the stability of the system.

Spectrum Analysis

The objective of the γ-ray spectrometry is to identify the radionuclides present in the sample and to quantitatively assay the radioactivity of each radionuclide. Though most of the radionuclides have unique γ ray energies due to their characteristic decay schemes, many times close lying γ-rays within the energy resolution of the system make it difficult to assign the Z & A of the radionuclide

unambiguously. In such cases the half-life is used to determine the radionuclide. The γ ray abundance values and half life values are available in the literature [3].

Peak Area Calculation

In the case of an isolated peak without any superimposed continuum, the peak area could be determined by simple integration. The continuum over which the peak is situated is assumed to be linear. However, in many cases the spectra are complex with overlapping peaks. In such a situation the peak fitting procedures are used. The data in the region of a peak are described by a sum of two analytical functions – the first represents the background and the second represents the peak.

The background is assumed to have a polynomial or step function.

$$\text{Step Background} = 1 \text{ for } x < X \qquad (8)$$

$$0 \text{ for } x > X$$

Polynomial Background = $(1/2)\text{erfc}[(x-X)/\sigma\sqrt{2}]$ (9)

Ideally the peak shape of lines could be represented by a Gaussian function

$$y(x) = \frac{y_0}{\sqrt{2\pi\sigma^2}} \ e^{-\frac{(x-x_0)^2}{2\sigma^2}} \qquad (10)$$

Where y(x) is the counts in the channel x and y_0 is the area under the Gaussian. x_0 is the centroid and σ is related to the FWHM (w) as w = 2.35σ. However in practice γ-ray peaks show tails on the lower and / or higher side of the centroid. The tails are represented by an exponential function. The standard computer codes like SAMPO, GAMANAL use Gaussian with or without lower exponential tail with background as polynomial or step function. The functional form used in SMPO is given below.

SAMPO

$$y(x) = e^{-\frac{(x-X)^2}{2\sigma^2}} \qquad \text{for } x > X - J \qquad (11)$$

The typical operations of the γ-ray spectrum analysis are,

(i)   Peak Find
(ii) Energy Calibration
(iii) Shape Calibration
(iv) Efficiency Calibration
(v)   Peak Fitting and area calculation
(vi) Activity Calculation.

Peak Find

The peak location is usually done by the second derivative method. The second derivative shows a large –ve peak and two smaller +ve peaks for a single γ ray peak and the peak location corresponds to the minimum of the –ve peak.

Energy Calibration

Standard multi gamma sources having γ ray energies encompassing the energy range of interest are used for this purpose. Precise measurements of X rays and low energy γ rays were carried out with curved crystal spectrometers and that of higher energy γ-rays by measurement of energy of internal conversion electron lines relative to the γ-ray. The standard energies used were 59.31918 keV $K\alpha_1$ line from tungsten for X-rays and 411.8044 keV γ-ray from ^{198}Au. Subsequently multi γ-ray sources like ^{152}Eu have become more common. Table-3 gives the nuclides and their γ-rays used for energy calibration. The functional form of energy calibration is,

$$E = a + b.ch + c.ch^2 \qquad (12)$$

Shape Calibration

The γ-ray peaks are fitted into the function of interest as described above and the FWHM is fitted into a polynomial of the form,

$$\text{FWHM} = p + q.ch + r.ch^2 \qquad (13)$$

The constants are stored in the memory and are used in the subsequent analysis.

Efficiency Calibration

Efficiency of detection depends upon the detector type, size and source to detector distance. The absolute efficiency (ε_γ) can be considered as the
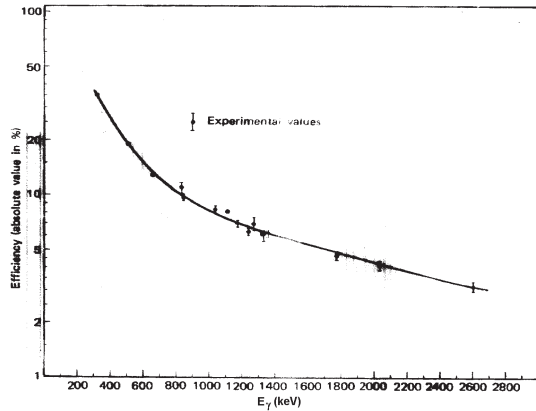
Fig. 1   Typical efficiency curve for a HPGe detector

product of geometric efficiency (ε_g) and intrinsic efficiency (ε_i).

$$\varepsilon = \varepsilon_g \cdot \varepsilon_i \tag{14}$$

$$\varepsilon_g = \frac{\Omega}{4\pi} = \frac{ds}{4\pi d^2} \tag{15}$$

Where ds is the Surface area of detector and d is the source to detector distance.

$$\varepsilon_I = 1 - e^{-\mu t} \tag{16}$$

Where μ is the linear attenuation coefficient for the detector material (Ge) and t = detector thickness. Above expression does not give correct results due to several factors, namely, (i)the detector thickness may not be known accurately, (ii) Compton Scattering and pair production do not lead to full energy deposition, (iii) dead layer in detector surface may attenuate low energy γ-rays. Therefore, the absolutely efficiency is usually determined by counting sources of known activity in standard geometry.

$$\varepsilon = \frac{cps}{dps \times a_\gamma} \tag{17}$$

A typical efficiency curve is shown in Fig. 2.

The radionuclides which are used as primary standards for efficiency calibration are given in Table 1. The measured efficiency data least square fitted into a function of the form,

$$\ell n\, \varepsilon_\gamma = \sum_{i=1}^{n} a_i (\ell n\, E_\gamma)^i \tag{18}$$

Where n can vary between 2 and 4.

Peak Area Calculation

The simplest way of peak area calculation is by adding the counts in the peak and subtracting the background, which can be assumed as linear.

Net peak area (N) = G – B   (19)

where L and H represent the lower and upper channel number of the region of interest of the peak.

Peak Area from Fitting

Peak area can be taken as the integral of the analytical function.

Activity Calculation

The activity (A) of the sample is calculated as

$$A = PA/(T.\, a_\gamma\, \varepsilon_\gamma) \tag{20}$$

In case of the counting time (T) being significant fraction of the half-life of the radio-nuclide the decay during counting has to be taken into account. In that case the activity at the beginning of the counting is given by.

$$\tag{21}$$

Error Calculation

In the case of simple peak area calculation the error on the net peak area is given by,

$$\sigma_N = (\sigma_G{}^2 + \sigma_B{}^2)^{1/2} \tag{22}$$

In the case of peak fitting procedure the fitting error also contributes to the peak area. The error on activity (A) is given by,

The main contributions to the uncertainty arise from,

(a) Statistics of the peak area which is the major source of uncertainty in low level counting.

(b) Efficiency Calibration.

(c) Reproductability of the source position with respect to detector for source and standard.

(d) Dead time and pile up correction of high count rates.

Table 1 - Primary calibration radionuclides used for efficiency calibration

Nuclide	Energy (keV)	Emission probability (%)	Half-life
^{57}Co	122.0614(3)	85.68(13)	271.79(9) d
^{139}Ce	165.857(6)	79.9(3)	137.640(23) d
^{203}Hg	279.1967(12)	81.56(8)	46.595(13) d
^{113}Sn	391.702(4)	64.89(17)	115.09(4) d
^{85}Sr	514.0076(22)	98.0(10)	64.849(4) d
^{134}Cs	604.69(2)	97.63(3)	754.28(22) d
^{137}Cs	661.660(3)	85.20(20)	30.25(11) y
^{54}Mn	834.843(6)	99.976(2)	312.3(4) d
^{60}Co	1173.238(4)	99.89(2)	5.2719(14) y
	1332.502(5)	99.983(1)	
^{22}Na	1274.542(7)	99.93(2)	2.603(2) y
^{88}Y	1836.063(13)	99.36(5)	106.630(25) d

(e) Photon attenuation correction in case of extended sources.

Coincidence Summing Corrections

Radionuclides emitting two or more γ-rays in cascade lead to coincidence summing. If both the γ rays of cascade are emitted in the same directions and deposit their energy in the detector volume, a sum pulse is recorded leading to loss of event from the full energy peak of both photons. The probability for coincidence summing increases with increasing total efficiency, that is, with decreasing source to detector distance but is independent of the count rate. Consider the decay scheme shown in Fig. 3.

In the absence of coincidence summing, the count rate of γ_1 is

$$n_{10} = A \, p_1 \, \varepsilon_1 \qquad (23)$$

If both γ rays γ_1 and γ_2 are detected simultaneously, the count rate of γ_1 is decreased.

$$n_1 = AP_1\varepsilon_1 - AP_1 \, \varepsilon_1 \, \varepsilon_2 W(\theta)$$

$$n_1 = AP_1\varepsilon_1 - AP_1 \, \varepsilon_1 \, [1\text{-}\varepsilon_2 W(\theta)] \qquad (24)$$

The correction factor is given by,

$$C_1 = n_{10}/n_1 = 1/[1\text{-}\varepsilon_2 W(\theta)] \qquad (25)$$
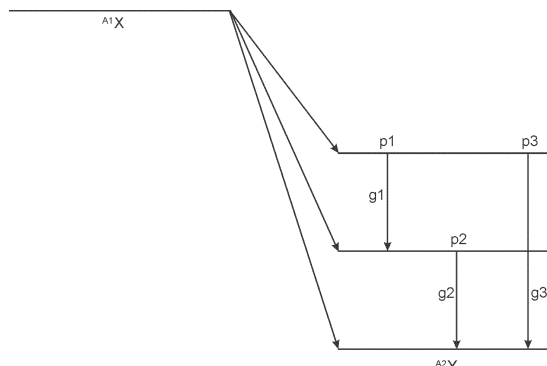
Likewise for the second gamma-ray,

$$N_2 = AP_2\varepsilon_2 - AP_2\varepsilon_2(P_1/P_2) \, \varepsilon_1 w(\theta)$$

$$= AP_2\varepsilon_2[1\text{-}(P_1/P_2) \, \varepsilon_1 w(\theta)] \qquad (26)$$

The correction factor for second gamma-ray is given by.

$$C_2 = n_{20}/n_2 = 1/[1\text{-}(P_1/P_2) \, \varepsilon_1 w(\theta)] \qquad (27)$$

P_1/P_2 is the fraction of γ_2 rays which are preceded by γ_1.

Fig. 3   Typical decay scheme of a radionuclide

Dead Time Correction

The finite processing time of the detector pulses in the spectroscopy amplifier and the ADC result in the finite dead time losses which increase with increasing count rate of the sample. Typical processing time in the spectroscopy amplifiers are of the order of 10 μsec which is about 3 times the shaping time. On the other hand the processing time in ADC is quite high. In Wilkinson type of ADC the processing time of the largest pulses may be of the order of 100 μsec and vary with the pulse height. In the ADCs of successive approximation type the processing time is constant and is of the order of several micro seconds. The dead time is equal to the time taken to process a pulse. Thus for a Wilkinson type of ADC the dead time for 1000 cps count rate will be,

$$T = 10^{34} \frac{Pulse}{Sec} \times 100 \times 10^{-6} \frac{Sec}{Pulse} = 0.1sec \text{ in 1 sec}$$

Most MCAs register the elapsed clock time (CL) and live time (LT) where,

$$CL = LT + \sum_{i}^{n} Ti \qquad (28)$$

n = no of pulses.

The average fractional dead time is given by, (CL-LT)/CL.

For a constant count rate source e.g. for a long lived radioisotope, live time mode takes care of the dead time losses. But in case of short-lived radioisotope the decay during the counting time results in variable dead time which is not easy to correct.

Recently a loss free counting system has come into market which offers the possibility of counting the samples having as high dead time as 90%. The system makes up for the dead time losses by taking very short acquisition time and applying a correction in real time. Conventional dead time correction is based on Gedke Hale method wherein the live time is extended to take into account the lost counts. Loss free counting mode corrects the data by adding extra counts to accounts for the dead time losses. Thus instead of the acquisition time the data are corrected [4].

Pile up Effects

The preamplifier and amplifier accept and process all the pulses originating in the detector and are not dead for a second pulse while processing the first one. If two pulses appear in the amplifier within the processing time for one pulse, the amplifier output is distorted and appears at a different voltage. The magnitude of the combined pulse depends upon the arrival time of the second pulse. If the two pulses come simultaneously the combined pulse is recorded at different channel no in the MCA from the original pulses height. In other cases when the second pulse comes after the first pulse right hand tailing of peaks occurs.

Most modern day spectroscopy amplifiers have electronic pile up rejection circuits. Usually the fast pulses generated at the amplifier are used for the purpose. The slow channel pulses, which are determined to be closely spaced in time can be rejected by turning off the ADC at the time they would reach it.

One of the post measurement methods of pile up correction is by measurement with a set of sources containing known relative amounts of different radionuclides of varying γ ray energy. If no pile up losses occur the ratios of the measured peak areas and the activity should be independent of the total count rate, provided the same analyzer live time LT is chosen each time. Any change in this ratio is an indication of pile up losses and the amount of this change can be used to derive a relationship between (pile up + dead time) losses and count rate.

Pulser Method

In this method a pulse is fed to the test input of the detector. The pulser output undergoes same processing as the γ ray pulse. The pulser and detector signals suffer the same fractional counting losses due to dead time and pile up effects. Since the pulser count rate is known, a comparison of the observed pulser peak count rate and actual pulser count rate gives the loss due to pile up and dead time effects. In some of the MCAs the pulser peak is recorded in an auxiliary spectrum so that its peak area can be computed accurately. Let the pulser count rate be C_p. The observed peak area of pulser peak (N_p) is less than the true counts ($C_p.T$). The correction factor for

any peak area would be $(C_p.T/N_p)$. Thus for any other γ-ray, the true count rate $N_0 = N(C_p.T)/N_p$. Where N is the measured counts.

Choosing a Detector

The choice of the detector depends upon the nature of application. For routine gamma-ray spectroscopic assay of radioactive samples and neutron activation analysis, a 30-40% p-type HPGe detector with aluminium window thickness, around 0.1 mm would be adequate. The range of gamma-ray energy of interest is usually 60 – 2000 keV. The energy resolution of such a system is around 1.8-1.9 keV at 1332 keV gamma line of ^{60}Co. For low energy (10-60 keV) gamma-ray measurements a low energy photon spectrometer (LEPS) consisting of a coaxial 5 cm^3 HPGe detector with 0.025 mm thick beryllium window would be ideal. The resolution of such a system is around 500 eV at 122 keV. This type of detector system is useful for measurement of isotopic composition of Plutonium samples.

Another commonly used HPGe detector is the LOAX, which is a planar detector and is sensitive to the gamma-ray energy range of 40-500 keV. For X-ray fluorescence (XRF) studies, Si(Li) detectors having much better resolution (150 eV at 5.9 keV) are used.

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Nuclear Analytical Facilities at the Indira Gandhi Centre for Atomic Research

Shri C.R. Venkata Subramani *joined the Department of Atomic Energy in 1976 through the 20th Batch of Training School. He is currently looking after Nuclear Chemistry and Non-Destructive Assay work in Fuel Chemistry Division of Indira Gandhi Centre for Atomic Research (IGCAR). His main areas of interest are applications of non-destructive assay techniques at various stages in the fast reactor programme and the reprocessing plant.*

The Indira Gandhi Centre for Atomic Research (IGCAR) formerly known as the Reactor Research Centre was set up with the mission of developing the necessary science and technology for the liquid metal cooled fast breeder reactors and its fuel cycle. In addition to the Fast Breeder Test Reactor, IGCAR also houses a research reactor KAMINI (KAlpakkam MINI reactor) and an accelerator facility. The nuclear analytical techniques are centered on the latter two facilities and this article summarizes the details of these facilities.

Reactor Based Facilities

Neutron Activation Analysis

KAMINI is a 30 KW, ^{233}U fuelled, demineralized light water moderated and cooled, beryllium oxide reflected low power research reactor and is being extensively used for neutron activation analysis. The irradiation facilities consist of a pneumatic fast transport system and two irradiation thimbles. The fast transport system ends in between the core and the BeO shield and the flux at this location is 10^{12} at full power. The size of the rabbit in the pneumatic fast transfer facility limit the amount of sample permitted to less than 2 g with cylindrical dimensions of 8 mm diameter and about 12 mm height. The flux at the thimble locations is lower by about an order of magnitude. The thimble locations use Harwell cans and hence dimension and weight limitations are determined by the dimension of the standard Harwell can. KAMINI also has a neutron beam facility. The flux in this position is around 10^6. This facility is available for radiation physics research like study of composite shields and evaluation of new detectors.

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Neutron Radiography

There are two beam ports in KAMINI which are exclusively reserved for neutron radiographic work. The reactor has been physically located directly beneath the hot cells of the Radio metallurgy laboratory to enable neutron radiographic work on the irradiated fuel and blanket sub-assemblies discharged from FBTR. The neutron radiography facility consists of a carriage and drive system to lower radioactive samples from the hot cell into the beam path. Other samples can also be analyzed for which sample holding and positioning system is available along with direct and indirect image recording films, real time radiography camera and image recording facilities.

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Accelerator Based Facilities

At the Materials Science Division (MSD), particle accelerator facilities providing ion beams in

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the energy range of several keV to a few MeV, exist for materials research. A 150 kV gaseous ion accelerator with post-acceleration mass analyzer and UHV implantation chamber has been extensively used for studies in the broad area of accelerator based material science and ion beam characterization of materials. In addition, a 400 kV heavy ion accelerator is also available. Recently, a 1.7 MV Tandetron accelerator with high beam current and heavy ion capability has been commissioned. This accelerator is equipped with a SNICS and a duo-plasmatron ion source which provides ion beams for practically all elements. One beam line at the tandetron accelerator has facility for scanning the beam over a large sample area for ion implantation / irradiation studies. Experimental setups for ion beam analysis work consisting of RBS, channeling, PIXE and Nuclear Reaction Analysis have been installed. A micro-beam line is being planned and will be commissioned soon. In addition, post-implantation material characterization tools exist in the centre. The accelerator based materials research program falls into two categories : (a) Studies on nano-clusters and ion beam analysis in semi-conductors and (b) Radiation damage studies with special emphasis on materials of relevance to the fast reactor program.

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Nuclear Analytical Techniques (facilities) at VECC, IUC, Kolkata

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Nuclear techniques, where the nuclear properties are exploited, have high sensitivity and accuracy and are important tools for chemical analysis. Analysis of ultra trace level using these techniques has importance in basic research and in many applications including geological prospecting, environmental contamination survey, biomedical investigations etc. Suitable nuclear radiations (α, β, γ, n) are measured to estimate the concentration of the radiation emitting isotope which in turn is used to determine the elemental concentration. Some of the nuclear analytical techniques that are being carried out at VECC and IUC are the following. Charged particle activation analysis (CPAA) using accelerated charged particle has particular importance when certain elements do not produce suitable gamma emitting isotope by neutron activation.

In certain situation of analysis an external source of radiation is used to produce secondary radiation from the sample. Elemental analysis is then done from the measurement of this secondary radiation. Particle induced X ray emission (PIXE), X ray fluorescence (XRF) are the measuring techniques that fall in this category. Scattering of charged particles from a sample surface can be used for the chemical analysis. Rutheford backscattering (RBS) is a versatile tecnique for the depth profiling of sample surface. Changes in electronic, geometric, magnetic, defect structure of a material can serve the basis of analytical application. Measuring techniques include different hyperfine techniques viz. Mosbauer spetroscopy (MBS), time differential perturbed angular correlation (TDPAC) etc. Separation of a desired species from a mixture can be done by using high performance liquid chromatography (HPLC) technique. It is possible to identify the species from the position of the peak and and its quantity can be obtained from the peak area.

Some of the facilitites available at VECC and IUC are briefly described below:

(a) Radiochemistry laboratory equipped with fume hoods and glove box provides facility for handling radioactive samples. Separation of the desired element can be carried out and then radioactivity can be measured by suitable measuring techniques mentioned above.

(b) Irradiation chambers for irradiation of different types of targets in the accelerator are available with accurate measurement of beam current with electron suppressed Faraday cup attached to the chambers. This is particularly required for the experiments in CPAA technique.

High Resolution Gamma Spectrometry

Radiochemistry and Analytical Chemistry laboratories, VECC and IUC, Kolkata have HPGe detectors with sizes varying from 10% to 25% with energy resolution ~1.8-2.0 keV at 1332 keV. PC

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based 8K multichannel analyser (MCA) is used for data acquisition and analysis.

XRF

A semiplanar n type Ge detector with sensitive volume of 1 cm^3 is available at RCD, VECC for low energy photon measurement. This has a Be entrance window of 40 μ thickness attached to a gate valve that can be opened to make it suitable for beta spetroscopy. This has energy resolution of 190 eV at 5.9 keV and 500 eV at 122 keV. An annular source of ^{241}Am is used as the excitation source. A PC based data acquisition system and the software axil is available for analysis of the X-ray spectra.

HPLC

A high performance liquid chromatography unit with Waters 501 pump and Waters U6K injector coupled to either Waters 486 tunable absorbance detector or a gamma detector [NaI(Tl)] is available at radiopharmaceuticals laboratory, VECC. Data acquisition and analysis is done with PC based software. A similar HPLC unit is also available at IUC, Kolkata.

An alpha spectroscopy setup with a surface barrier detector is available at RCD, VECC. This has an energy resolution of 14 keV at 5156 keV.