Nuclear Techniques in Research

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Editorial

On behalf of the executive committee, I apologize to our esteemed members for the delay in publishing this bulletin. Today, the boundary between various disciplines is fast vanishing and a multi-disciplinary approach to research is the in thing. This requires an exposure to a variety of subjects and experimental techniques for a researcher, specially the young research scholar. In view of this, we want to make a beginning in disseminating a variety of information through this bulletin and intend to devote each issue to a particular subject, so that the reader(s) gets a comprehensive knowledge on it. The present issue contains four articles on nuclear techniques which are application oriented. Hope you will enjoy reading them.

We believe, that our bulletin could also serve as a platform for exchanging views and can help towards a stronger interaction between members. We propose to publish, along with regular articles, brief abstracts of thesis of research scholars (not exceeding 500 words), views of individual members through a column "Letters", news items in science and technology and any other feature/information that will enrich the bulletin. Members are also requested to communicate to us any awards/distinction achieved by them or any other news they wish to share with others.

I appeal to you for suggestions to improve the quality of this bulletin as well as looking forward to your contributions for the same. I thank all the authors for their prompt response in contributing the articles for this issue.

I take this opportunity to wish you all Happy Diwali.

S.B. Manohar

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Positron Annihilation Spectroscopy: Application in Multi-Disciplinary Research

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Introduction

The discovery of positron in 1930 and subsequent developments have led to a new spectroscopy namely positron annihilation spectroscopy (PAS), which has quickly expanded across interdisciplinary areas. Besides thermodynamics, kinetics, biochemistry, quantum chemistry, radiation chemistry, analytical chemistry and solid state chemistry, positron has also made contact with electron scattering theory and experiments, biophysics and medicine and the basis of quantum electrodynamics. This article covers the basic principles of this technique and briefly delineates a few multidisciplinary applications.

Positrons are commonly obtained through pair production of radioactive decay of neutron deficient radioisotopes e.g. ^{22}Na, ^{64}Cu etc. When the energetic positron is injected into a medium, it thermalises in a few picoseconds, much shorter compared to its intrinsic life-time. Then the positron annihilates with an electron giving two 511keV gamma photons emitted in opposite directions. The positron may also form a stable bound species with an electron called positronium (Ps), especially in molecular solids, liquids and gases. The PAS is devoted to monitoring the emitted annihilation photons giving information about the electron momentum distribution and electron density at the annihilation sites which in turn reflect the physico-chemical properties of the material under study.

Experimental Techniques

There are mainly three experimental techniques, namely, Angular correlation of annihilation radiation (ACAR), Doppler broadened annihilation radiation (DBAR) and life-time spectroscopy (LTS). We know that the two annihilation photons (511 keV) are emitted in opposite direction. This is true if the electron-positron pair momentum is zero, else, the energy and momentum conservation brings about an angular deviation from 180° in the emission direction of the annihilation photons, θ, which is a measure of the electron-positron pair. Since at the time of annihilation the positron is thermalised or its kinetic energy is in the order of meV, the contribution to the electron-positron pair momentum comes primarily from the electron and hence the angular deviation is directly related to the electron momentum as

$$\theta = p / mc \qquad (1)$$

Where p is the electron momentum, m and c are the mass of electron and velocity of light respectively. Thus by measuring the number of annihilation events as a function of angle, the so called angular correlation, one obtains the momentum distribution of electron in any medium.

DBAR technique essentially gives the same information as ACAR. The annihilation photopeak undergoes Doppler broadening due to the momentum (or kinetic energy) of electron-positron pair. This broadening is the measure of the electron momentum and given as

$$E = \pm pc/2 \qquad (2)$$

The instrument used for this is a high resolution gamma ray spectrometer.

Life-time spectroscopy on the other hand involves the measurement of the time interval between the birth and death of a positron in any medium, the inverse of which is the decay rate and is directly proportional to the electron density at the annihilation site as

$$\lambda = r_0^2 \cdot c \cdot n_{el} \qquad (3)$$

Where λ is the decay rate, r_0 is the classical electron radius and n_{el} is the electron density. ^{22}Na source is taken as positron source where the emission of a positron is associated with emission of 1275 keV gamma ray serving as start signal. The annihilation photon is taken as stop signal and a fast coincidence circuitry is used to accomplish these measurements.

In addition to these three, there is other which is either extension of one of these or a combination of more than one, providing specific correlated information. They are: Two dimensional Angular Correlation (2D-ACAR) and Multiparameter Measurement technique respectively. In recent years, positron beam technique is utilized in studying various physico-chemical phenomena in solids.

The observed spectra in ACAR and DBAR are described by various shape parameters, more often by S-parameter, which is the ratio of central area to the total area of the peak. Any change of state of matter reflects in the positron annihilation parameter and hence PAS is a powerful diagnostic tool in solid state research as well as liquid and gaseous states.

Application

Electronic Structure of Ideal Metals

The electron in simple metals can be roughly divided into nearly free valence electrons and tightly bound core electrons. The presence of dense electron gas totally prevents Ps formation. The repulsive interaction between the positrons and the ions results in small overlapping of the positron and core electron wave functions. Thus the annihilation rate, obtained through LTS, is almost totally determined by the valence electron density.

The angular distribution of annihilation radiation-ACAR-(also DBAR) gives the momentum distribution of the electrons in the metal. This distribution consists of two parts, the inverted parabola and a broader Gaussian, contributed by the free electron and the core electron respectively. The intersection of these two parts directly gives the Fermi angle corresponding to the Fermi momentum. Measuring the momentum distribution in two planes simultaneously, using 2D-ACAR, gives Fermi surface.

Defect Studies

The behaviour of positrons in simple metals is quite well understood as described earlier. However, it was seen that various physical states of the metal can drastically change the annihilation properties. In the deformed solids or in the presence of defects, the positrons are trapped, because, in the disordered region the positive charge (of ions) is reduced and the resulting redistribution of electrons leads to a net negative electrostatic potential attractive to positron. The electron density at the site of the defects is smaller and consequently the positron life-time increases. The same reason also leads to the narrowing of the angular correlation curve and Doppler broadened annihilation photopeak which is reflected in the S-parameter. The extent of the changes in the life-time or S-parameters depends upon the concentration and nature of the vacancy or defects. By using positron the following information on defect properties can be obtained.

Concentration of defects can be deduced from the ratio of free and trapped positrons. The advantages of the positron method lie in the fact that its sensitivity starts already from the vacancy concentration of about ppm level. This can also give vacancy formation and vacancy migration energies. This is achieved by measuring any positron annihilation parameter as a function of temperature.

The annihilation characteristics of trapped positrons reflect the local properties of defects, thus giving unique information on their internal electronic structure.

The annihilation characteristics of trapped positrons are to some extent different for different defect configures e.g. they can reveal vacancy agglomeration and give estimates on the size of micro voids which are too small to be detectable by any other method. Studies in defect aspects in solids are probably the most developed area in positron research.

Surface Studies

One of the most exciting areas of research today is the field of surface and interfacial phenomena. The surface chemical processes occurring at the solid-solid, solid-liquid and solid gas interfaces are very interesting and now PAS has

established itself as an in-situ analytical technique in characterizing the surface of solids and the chemical and physical changes of adsorbed molecules on it. The annihilation rate dependence on surface area, size of void, specific reaction characteristics of positron with different gases are exploited to obtain these information's. In addition, hidden surfaces or pores (specially in catalysts) can also be characterized using this technique due to easy accessibility of positrons into these pores or hidden surfaces. Of late positron beam technique has been utilized to probe surfaces and interfaces obtaining unique information about their electronic properties.

Other Applications

As described earlier, the positron annihilation parameters respond to a fluctuation in case of change of state of matter. This feature has been extensively exploited to probe various phase transition phenomenon e.g. structural phase transition, melting and boiling point, order-disorder transition etc. Among other significant applications the study of micro structural properties in polymers and catalysts, study of colour centres, study of gas diffusion mechanism in metals and many others (See References). Another potential application area is the study of molecular association process e.g. micelle formation and characterization, determination of formation constant where both the reactant and product absorb at the same wavelength. The latter process has been studied extensively in biological systems. Study of membrane phase transition, interaction of electron-transfer molecules in membranes, micro structural information of membrane are some of other interesting applications in biological systems. One of the most interesting and challenging application of PAS in recent years is on the high temperature superconductors and it has made considerable contribution towards understanding this exciting phenomenon.

To conclude, PAS is a qualitative, non-destructive and in-situ probe and capable of providing valuable information in several areas. As it is clear from the above discussion, this technique has made its mark in solid state physics and chemistry. The future of PAS is its potential for becoming an analytical tool in chemistry for which the foundation is just laid and researchers in interdisciplinary areas should take advantage of this probe, enriching their respective fields as well as helping realize a mature tool called Positron annihilation spectroscopy for chemical analysis (PASCA).

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Perturbed Angular Correlation

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Perturbed angular correlation (PAC) is a nuclear technique useful for studying extranuclear electric or magnetic fields around the probe nucleus. The technique derives its potential from the interaction of nuclear magnetic dipole moment with surrounding magnetic field or that of the nuclear electric quadrupole moment with extranuclear electric field gradient (EFG). The field may be due to the atomic electrons, ions in the crystal lattice or the long range magnetic ordering. These hyperfine interactions are well known in techniques like nuclear magnetic resonance (NMR), electron spin resonance (ESR), atomic spectroscopy, Mossbauer spectroscopy etc. While these latter techniques have expanded to a large extent over the past few decades, PAC has been limited to nuclear scientists for the following reasons.

(i) Unlike in NMR and other techniques mentioned above where commercial push button instruments are available in market, the PAC instrument has to be set up by the experimentalists themselves. This requires adequate knowledge of nuclear instrumentation and associated electronics.

(ii) Secondly there are only a few nuclides which can be used as nuclear probes. Though in solid state physics/chemistry studies one can find a suitable probe for doping in the sample, the same cannot be tried in case of chemical applications. Table 1 gives the list of probe nuclei along with the relevant nuclear spectroscopic data.

Despite these limitations PAC today finds wide applications in diverse fields, such as, solid state physics/chemistry, nuclear physics, chemistry, biology, etc. and its usage is increasing with experimentalists becoming aware of the associated electronics set up for PAC. Further, the PAC technique has some advantage over other hyperfine tools, namely,

(i) Unlike in NMR and Mossbauer spectroscopy, where in the sample has to be in macroquantities, there is no limitation on sample amount in PAC and even trace levels of samples can be studied.

(ii) PAC can be applied to solids, liquids and gaseous samples without any difficulty unlike in other techniques.

The present article starts with a brief account of the theory of PAC followed by some of the applications.

Theory of PAC (1)

Let us consider a radioactive isotope (A) decaying by alpha or beta decay to the excited state of the daughter product (B). The excited state with spin I_i then decays by a cascade of gamma rays to the ground state having spin I_f. The intermediate state has the spin I. the two gamma rays r_1 and r_2 follow a definite angular correlation depending upon the spin states (I_i, I and I_f) and the multipolarities of the gamma rays. Thus if we record the two gamma rays in two NaI(Tl) detectors, the coincidence counts between r_1 and r_2 is given by,

$$W(\theta) = 1 + \sum_k A_{kk} P_k (\cos \theta) \qquad (1)$$

where A_{kk} are the radiation parameters which depend upon the spin states and multipolarities of the gamma rays and $P_k (\cos \theta)$ is the Legendre polynomial of kth order. In practice the higher order terms are negligible compared to k=2 term and therefore equation 1 can be simplified as,

$$W(\theta) = 1 + A_{22} P_2 (\cos \theta) \qquad (2)$$

This is known as the unperturbed angular correlation function.

Now consider that the intermediate state (I) has a finite lifetime (τ) and then during this time the

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Table 1. PAC probe nuclei and their spectroscopic data

Nuclide	Half-life	Life time (nano secs)	E1 (keV)	A1 (%)	E2 (keV)	A2 (%)
^{44}Ti	48Y	153	78	100	68	100
^{99}Rh	16d	21	354	20	90	80
^{100}Pd	3.7D	214	84	70	75	70
^{111}Ag	7.5D	84	95	0.5	247	1
^{111m}Cd	49M	84	150	100	247	100
^{111}In	2.7D	84	173	100	247	100
^{117}Cd	2.4H	60	89	7	345	16
^{131m}Te	30H	5.9	102	5	200	10
^{181}Hf	42D	10.8	133	93	482	85
^{187}W	24H	560	480	30	72	15
^{199m}Hg	43M	2.3	375	100	158	100
^{204m}Pb	67M	260	912	98	375	99
^{204}Bi	11H	260	984	20	375	90

nuclear electric quadrupole moment (Q) or magnetic dipole moment (μ) may interact with the surrounding field thereby altering the angular correlation.

$$W(\theta) = 1 + A_{22} G_{22} P_2 \ (\cos \theta) \qquad (3)$$

where G_{22} is the perturbation factor and it gives the information about the surrounding fields. The interaction of the extranuclear electric (magnetic) field with Q (μ) lifts the degeneracy of the magnetic sub states of the intermediate state (I). The hyperfine interaction essentially induces transition among these sub-levels analogous to that in NMR or Mossbauer spectroscopy. In order to have a non-zero Q (μ) the intermediate state must have spin ≥ 1 (1/2). In the following discussion I shall restrict myself only to electric quadrupole interaction between the nuclear quadrupole moment and the extranuclear electric field gradient (EFG).

PAC can be used in time differential or integral mode depending upon the resolving time of the PAC setup as well as the interaction time. The instrumentation is a slow fast coincidence set up using NaI(Tl) detectors.

Time Differential Perturbed Angular Correlation (TDPAC)

In this technique the angular correlation between the two gamma rays is measured as a function of the time delay between the emission of r_1 and r_2. As the intermediate level has a finite lifetime (τ) (for PAC a τ of few nanoseconds to hundreds of nanoseconds is required) in the case of unperturbed angular correlation the $W(\theta)$ will follow an exponential decay with slope equal to $1/\tau$. However in the presence of the perturbation the $W(\theta)$ will show oscillations as a function of time. By measuring the $W(\theta,t)$ at two angles, say 90° and 180°, one can calculate the perturbation factor $G_{22}(t)$ as,

$$G_{22}(t) = \left(\frac{2.\,W(180,t) - W(90,t)}{W(180,t) + 2\,W(90,t)} \right) \qquad (4)$$

The functional form of G_{22} depends upon the type of interaction that is whether the interaction is time dependent or static. In case of gaseous samples or dilute solutions the perturbation relaxes very fast due to the molecular rotation and the perturbation factor is expressed as,

$$G_{22}(t) = \exp(-\lambda_2 t) \qquad (5)$$

where λ_2 is the relaxation constant and it depends upon the molecular size and the interaction frequency.

For solid samples the interaction between Q and EFG is static and the perturbation factor is given by,

$$G_{22}(t) = \sum_{n=0} S_{kn} \cos w_n t \qquad (6)$$

where ω_n's are the frequencies corresponding to the transitions among the m substates of the intermediate level. For an axially symmetric EFG the ω_n's are integral multiple of the fundamental frequency (ω_o) which is related to Q and the Z-component of EFG (V_{ZZ}) by,

$$\omega_o = \frac{eQV_{ZZ}}{4I(2I-1)} \qquad (7)$$

Thus TDPAC can give detailed information about the EFG around the probe nucleus.

Integral Perturbed Angular Correlation (IPAC)

If the resolving time of the PAC setup is larger than the interaction time $(2\pi/\omega)$ then TDPAC measurements cannot be made. However one can still get the average value $<q_Q^2>$ by integral measurements. In this method the total coincidence counts at an angle, that is, $W(\theta, \infty)$ are measured and the $G_{22}(\infty)$ is obtained using the equation analogous to 4, with t replaced by $G_{22}(\infty)$ is now given by,

$$G_{22}(\infty) = \left(\frac{1}{\tau}\right) \int G_{22}(t) dt \qquad (8)$$

For the time dependent interaction this can be simplified to,

$$G_{22}(\infty) = \frac{1}{(1+\lambda_2 \tau)} \qquad (9)$$

The relaxation constant λ_2 is given by,

$$\lambda_2 \, \alpha \left\langle \omega_Q^2 \right\rangle \tau_c \qquad (10)$$

where τ_c is the correlation time which is a measure of the rotational time of the molecular species and is given by,

$$\tau_c = \frac{\eta V}{kT} \qquad (11)$$

V is the volume of the molecule and η is the viscosity of the solvent at temperature T. Thus IPAC measurements in solutions can be used to determine the size of the molecular species.

Applications of PAC

The PAC technique is today widely used in solid state physics and chemistry, chemical problems, biology and other fields. As this is not a review article, I have chosen a few examples in each of these topics to give a glimpse of the potential of PAC in different fields. A comparative review of the literature on application of PAC can be seen in reference (2).

Solid State Physics and Chemistry

The PAC technique has been widely used in the study of magnetic interaction in insulators, electric quadrupole interaction in insulators, hyperfine interactions in metals and alloys, static electric field gradients in ferro and anti ferroelectric perovskites, fluctuating EFGs in metals, spin fluctuations in inter-metallic compounds, high temperature superconductors etc. The literature on the Pac studies in these fields has been reviewed by Rinneberg (3).

PAC technique is quite sensitive to any structural phase transition in a compound. As an example the various phase transitions occurring in ferroelectric and anti ferroelectric perovskites such as $BaTiO_3$ and $PbHfO_3$ lead to corresponding changes in EFG. These phase transitions can be conveniently investigated by PAC using [44]Ti and [181]Hf as probes. The compound $BaTiO_3$ when studied (4) using [181]Hf as a probe showed step wise increase in EFG at 193 K, 273 K and a sharp fall at 378 K corresponding to the phase transition from rhombohedral → monoclinic → tetragonal → cubic phases. The compound becomes ferroelectric at 378 K. Because of the cubic symmetry of the paraelectric phase, the EFG drops to zero at the ferroelectric – paraelectric transition temperature.

The intermetallic compounds $Hf_{1-x}Ta_xFe_2$ with hexagonal laves phase structure are itinerant electron systems which undergo first order

ferromagnetic to anti-ferromagnetic transition for $0.15 < x < 0.2$ before attaining paramagnetic state and for $x=0.15$ this transition occurs at 250 K. TDPAC studies have been carried out (5) for $Hf_{0.85}Ta_{0.15}Fe_2$ at 77 K and 298 K. the perturbation factor at 298 K shows an exponential decay and analysis of the data gave $\omega_Q = 33 \pm 3$ MHz and the internal hyperfine field almost zero. Unlike this the 77 K data clearly shows oscillations in the perturbation factor corresponding to an internal hyperfine field of 19.3 ± 0.5 kOe. The analysis of 77 K data favours the spin orientation in C-plane.

The intermetallic compounds ZrNi and Zr_2Ni are of immense technological importance as they can absorb large concentrations of hydrogen. One is interested to know the rate of diffusion of hydrogen in these compounds. The otherwise static quadrupole interaction becomes time dependent owing to the diffusion of hydrogen. The diffusion of hydrogen in the crystallized hydride $Zr_2NiH_{3.8}$ has been studied by TDPAC (6) using ^{181}Hf as a probe which substitute Zr in this compound. The temperature dependence of the quadrupole relaxation between 200 K and 470 K could be described by assuming that the jump probability of hydrogen atoms results from the co-existence of two thermally activated processes.

Chemistry

PAC has not been a common technique to chemists due to reasons cited earlier. However for the past one and half decade there has been a spurt in the applications of PAC to chemical problems. Adloff has reviewed the chemical applications of PAC (7). PAC has been used to carry out structural investigations on inorganic compounds, complexations, polymerization, hot atom chemistry, radiation damage studies, etc.

An interesting study of hafnium fluoride was carried out by Bruin et al (8). They dissolved $HfOCl_2$ in 0.1 N $HClO_4$ and carried out IPAC measurements. The solutions showed a A_2G_2 (∞) value close to the hard core value of 0.2, that is, strong perturbation. Addition of a small amount of fluoride increased the G_2 rapidly which became unity for F^- / Hf ratio equal to six. Any further addition of F^- ions and the complex has cubic symmetry. This shows that (i) Hf is complexed by six F^- ions and the complex has

cubic symmetry. The cubic symmetry of the complex gives rise to zero EFG and hence no perturbation.

Hafnium complexation by ethylene diamine tetra acetic acid (EDTA) has been studied by Das et al (9). Samples of different Hf : EDTA ratios were prepared by adding EDTA solutions of known concentrations prepared in 4.6 M $HClO_4$. The samples were counted by IPAC method. It was found that the A_2G_2 (∞) decreases initially and saturates at a Hf : EDTA ratio close to unity. The stability constant of the complex Hf EDTA was also obtained. TDPAC of polycrystalline Hf EDTA was carried out to determine the quadrupole interaction frequency and the asymmetry of the EFG in the complex. There are several studies on Hf (IV) complexes with various ligands. TDPAC of the Hf (IV) complexes (10) with ligands e.g. tropolone, cupferon and N-benzoyl n-phenyl hydroxylamine (NBPHA) show that the quadrupole coupling parameters are sensitive to the nature of covalent ligands.

As I mentioned earlier the perturbation factor for liquid samples is sensitive to the size of the molecular species present in the sample. This makes PAC a useful tool to study the polymerisation in solutions. The polymerisation of Hf (IV) in different acids over a wide range of hydrogen ion concentration has been studied by IPAC (11). At higher acidity the hafnium species remain as monomeric and the degree of polymerisation increases rapidly as the acidity decreases. The observed behaviour was attributed to the existence of polymeric species heavier than the tetrametric form at lower acidity. The degree of polymerisation was found to be independent of the acid anion.

Biology

Very recently PAC has found wide applications in biology. These applications have been mostly centered around the structural aspects of different biological molecules with metal ions e.g. In^{3+}, Hf^{4+} Mo^{6+} etc. Recently, ^{99}Mo has been used (12) as a probe to investigate, through PAC technique, the interaction of ^{99}Mo (β^-) ^{99m}Tc in nitrogenase of the bacteria Klebsiella pneumonia. Study showed very high affinity of the bacteria to Tc

if no Mo-carrier was added. Even in the case of Mo carrier was present ^{99m}Tc enrichment was observed.

From above discussion it is quite clear that the PAC technique can give valuable information about the extranuclear electric as well as magnetic fields and thereby reveal the underlying phenomena. Considering the advantage it has over other technique, not withstanding the limited number of probe nuclei, it is hoped that PAC will find a wider application in several disciplines of science.

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X-ray Emission Spectrometry

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Elemental analysis is an important requirement of the industry for product development and process control. The presence of elements in very small amounts in chemical and biological systems as well as nuclear materials has great influence on their properties. Determination of elements by wet chemical techniques which often required days or weeks can be done in a few minutes by modern instrumental methods. X-ray spectrometry or X-ray fluorescence is an emission spectroscopic technique that has found wide applications in elemental identification and determination. X-ray spectrometry is quite versatile, since it can analyze all the elements in the periodic table down to $Z = 9$ (fluorine) in major and minor constituents. It can analyze solid or liquid samples independent of its composition or oxidation state and is non-destructive in nature.

X-rays are electromagnetic radiations, generated from the disturbance of electronic orbitals of atoms and is accomplished by the bombardment of a target element with high energy electrons, X-rays or accelerated charged particles. If the energy of the incident radiations is less than the binding energy of electron in a particular atomic level of the target atom, X-ray spectra result in the form of continuous radiation, which is termed as continuum or bremsstrahlung. The characteristic X-rays are emitted if the impinging energy is sufficient to knock the electrons from the inner atomic levels followed by the filling of the vacancy from the higher levels. Compared to the emission spectra observed in the visible or ultraviolet regions, x-ray spectra are quite simple due to the transitions between the limited energy levels of the innermost electrons in the atom.

The basis of X-ray spectrometry is Mosley's law which states a simple relationship between the wavelength (λ) of the characteristic radiation emitted and atomic number of the element (Z), as $1/\lambda = K (Z-\sigma)^2$ where K and σ are constants depending upon the spectral series. Elements present in the sample are identified from the wavelengths (or energy) of the characteristic lines present in the emitted spectrum, and their proportions are determined from the relative intensities of the selected line for each element, compared to emission intensities from the same elements in one or more calibration standards of known composition. There are different ways of excitation and dispersion of the X-ray spectrum. Depending upon the mode of excitation and dispersion of the X-ray spectra in the sample, X-ray spectrometric methods are classified as wave length dispersive or energy dispersive.

In the wave length dispersive spectrometers (WDS) excitation is done by the conventional X-ray tubes to excite secondary X-rays from the sample. X-ray tubes give both continuum and characteristic X-rays and both are useful for the excitation of the X-ray spectra in the sample. X-rays emitted from the sample are made to impinge on the surface of an analyzing crystal, which disperses the radiation. The polychromatic X-rays are diffracted from the crystal, which at an angle θ according to Bragg's law $n\lambda = 2d\sin\theta$, where 'λ' is the wavelength and 'd' is the interplaner spacing of the analyzing crystal and n is the order of reflection. LiF crystal with $2d = 4.028$ A is the commonly used analyzing crystal. This angular dispersion of radiation permits sequential or simultaneous detection of X-rays emitted by elements in the sample. The intensities are measured using wave length dispersive x-ray spectrometry by setting the goniometer at the '2θ' angle for the element of interest and counting x-ray pulses. A scintillation or proportional (sealed or gas flow) counters are used to convert X-ray photons into counts with the help of electronic system. The quantitative determination of elemental concentration is based on the relationship between the intensity of X-rays emitted by an element in the sample and concentration of that element in a thick

sample or on total amount of the element in an infinitely thin sample.

Energy-dispersive spectrometry (EDS) became established with the development of Si(Li) solid state detectors. Because of good resolution of Si(Li) detectors, EDS system required no dispersing crystal and hence none of the mechanical components required to maintain Bragg relationship in WDS. In the energy dispersive spectrometers, the detector receives the undispersed secondary beam comprising of all excited lines of all specimen elements. The amplified detector output is then subjected to pulse height analysis in the same way as that in λ spectrometry and the resultant pulse height spectrum is then obtained on a multichannel analyzer. Standard softwares for location of peak and calculation of peak areas are used to obtain the required data. The mean energy of the photopeak obtained is characteristic of the element (in the same way as wavelength λ) and the intensity or the peak area is proportional to the concentration of the element. The exact identification is carefully done by the known relation between intensities of K_α and K_β lines to avoid errors due to interferences. The excitation source can be a suitable radioisotope with low energy e.g., [241]Am (60 keV), [238]Pu (45 keV) etc. or as they have higher energies and suffer less attenuation in the sample and the window of Si(Li) detector. Only in cases of heavy elements such as isotopes of Pu, Am and Cm. where the emission of X-rays is a natural consequence of the radioactive decay 1-lines which are in the energy range of 15 to 20 kev have been used without external excitation sources. Particle induced X-ray emission (PIXE) uses x-ray beams of energetic ions, normally protons of 2-5 MeV, to generate X-rays from the specimen. PIXE has become an established analytical technique for the analysis of environmental and biological samples. The great advantage of the PIXE method over other sources is that it generates only a small amount of background and thus synchrotron radiations which are tunable, polarized and highly intense have been used as a primary source for X-ray emission and minimum detection limits of the order of picograms have been reported using them.

The qualititative information available from an X-ray spectrum is the energy or wavelength at which X-ray emission lines appear in the spectrum. The

quantitative information is the intensity of these emitted X-radiation. The intensity is normally expressed as the number of counts which are plotted vs. the concentration of the respective analyte element in standards to get a calibration curve. The relationship between intensity and concentration in X-ray spectrometry often depends upon on the total sample composition rather than only the element of interest, this is a result of matrix effects. Such cases require simultaneous or iterative computations of data for many elements in the sample by taking into account mass absorption coefficients.

Both the WDS and EDS techniques have certain advantages and limitations over the other and at best may be considered complementary to each other. For resolution, EDS is better at shorter wavelength (higher photon energies), and WDS is better at longer wavelength (lower energies). For qualitative analysis, EDS may be more advantageous, since it is rapid and convenient, but weak peaks may be unresolved if situated near strong peaks, and resolution is poorer at longer wavelengths. For the analysis of large number of analytes, EDS may be more useful since all the data are accumulated simultaneously. WDS is advantageous for measurement of individual analytes because only one analyte line enters the detector at a time.

For the quantitative assay of elements using both the technique the accuracy depends upon the close reproduction between the sample and standard and in the relative stopping power, which in turn depends on uniformity and thickness and this particular aspect requires ingenuity as well as skill of the experimenter.

X-ray emission spectrometry finds application in different disciplines. In cement industry elements like magnesium, aluminium, silica, sulphur, calcium, iron and potassium are routinely analysed using X-ray spectrometers. The BTU and ash content of a coal are estimated from its mineral composition. X-ray spectrometry is employed as a rapid and economical technique for determining major and minor elements in coal. EDS with its multiple element analysis capabilities, is ideally suited for many analytes of petroleum products. X-ray spectrometry is useful for rapid, on-line measurement to film thickness and composition in a

variety of coating and plating products. In the nuclear industry, the analysis of major and minor constituents of the fuel material is also done by X-ray spectrometry. Atmospheric physics and chemistry, external proton milliprobes and historical analysis are some of the areas where PIXE technique is quite useful. The high sensitivity of PIXE has been to great use in the field of forensic and in medicine. Applications include in vitro analysis of iodine in thyroid, lead in skeleton and cadmium in the kidney.

To summarise, an attempt has been made to introduce one of the modern and powerful analytical technique based on X-ray emission spectrometry. With better excitation sources and better detection systems as well as on line computation facility this particular technique has a bright future and total exploitation of this technique is a challenge to nuclear and analytical chemists.

Gamma Ray Spectrometry : Assay of Radioactivity In Environment

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Introduction

Since 1950, the effort for harnessing nuclear energy has gathered momentum and a number of power reactors have come up globally. Today more than 425 power reactors are operating and barring two major scars, the safety records of 5600 reactor years of these reactors is something to be proud of. The accidents at Three Mile Island in 1979 and at Chernobyl in 1986 have globally increased in public and government awareness regarding the release of radioactivity to the environment. The nuclear energy programmes were already aware of the effects of possible release of radioactivity to the environment even during the normal operations of reactors. The need to assess the levels of activity becomes all the more acute if the radioactivity in question finds its way in to the human body through food chain.

The mining and chemical processing of the uranium ores, fuel fabrication, reactor operations, fuel reprocessing of the irradiated fuel to separate plutonium and waste disposal are the major steps involved in the nuclear energy programme. At each of these steps, certain release of radioactivity to the environment becomes unavoidable. For the health considerations of not only the concerned work force but the public at large, the international body, IAEA, sets the limits on release of radioactivity and recommends the same to the member states. These limits depend on the biological half lives, energy deposited, type of radiation, organ specificity of the element, process of biological concentration etc. and keep a check on the radiation effects on human beings. It is but natural, that the limits are periodically updated. Adhering to these or even more conservative limits proves to be economical in long run if social cost involved is included in the cost benefit analysis.

Many methods for assessment of the levels of radioactivity in the environmental samples have been standardized. Present article discusses the principles and requirements of gamma spectrometric assay method. Results of some of our measurements on grass samples after the Chernobyl accident and the detection limits are also presented here as an illustration of this technique.

Radionuclides of Interest

Although several hundred radionuclides get produced in the reactor operations or nuclear explosions, only a few of them are of significant concern from the viewpoint of human exposure or the food chain. These radionuclides owe their origin to either fission or neutron activation process. The nuclides like ^{3}H, ^{54}Mn, ^{55}Fe, ^{60}Co, ^{65}Zn, ^{90}Sr, ^{95}Zr, ^{95}Nb, ^{103}Nb, ^{103}Ru, ^{106}Ru, ^{110m}Ag, ^{125}Sb, ^{131}I, ^{134}Cs, ^{137}Cs, ^{144}Ce, $^{238-240}$Pu and ^{241}Am can find way to the human food chain through the pathways like water, soil, vegetation, milk, marine life, crops and meat.

Principles of Gamma Spectrometry

The important advantage of gamma spectrometry over other methods derives from its ability to measure the samples directly without any cumbersome and time consuming chemical processes. Whereas, the main disadvantage of this method is that the pure beta emitters like ^{3}H and ^{89,90}Sr are not amenable to gamma spectrometric assay, $^{238-242}$Pu and ^{241}Am activity in the environmental samples is very difficult to assay due to long half lives and very low branching intensities of the gamma signature lines.

The estimation of activity A_i, of a radionuclide expressed as B_q/Kg of a sample, weighing W kg, is based upon the measurement of the photo peak area, P_i, of the signature gamma line for a counting

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Table 1 - Comparison of major contributions to the background spectra

Sl. No.	Setup contributions due to	Counts 1000/Sec.	
		80 cc HPGe	100 cc Ge (Li)
1.	Decay chain products of ^{238}Pu (^{214}Bi, ^{214}Pb, ^{234Th} and ^{234}Pa)	130	100
2.	Decay chain products of ^{232}Th (^{28}Ac, ^{212}Pb, ^{21}Bi and ^{208}Tl)	220	130
3.	^{40}K	48	107

duration of T seconds and is expressed by equation (1).

$$A_i = P_i / (T * W * B_i * Eff_i) \qquad (1)$$

where B_i is the branching intensity and Eff_i is the counting efficiency in a standard source to detector geometry for the gamma line of interest. The minimum detectable concentration (MDC) of a radionuclide in a sample is given by equation (2).

$$MDC = 4.66 * S / (Eff_i * B_i * W) \qquad (2)$$

where S is the standard error on net count rate and W is the weight of the sample in Kg. To obtain lower value of MDC the counting efficiency, weight of the sample and the counting time should be as large as possible. The practice of preparing the standards for efficiency calibration and samples in identical fashion takes care of attenuation corrections.

Large Volume Low Background Gamma Spectrometry

Since the photo peak area, P_i, is obtained by subtracting the Compton background from the gross area, the statistical errors on the accumulated counts heavily depend upon the Compton background. As a result, reduction in the background of a high resolution counting system improves MDC and helps in avoiding the masking of weak gamma lines by the background continuum. Most of the gamma lines contributing to the background are due to decay chain products of ^{238}U and ^{232}Th found in construction materials, presence of radiogenic lead isotopes in the lead shield, ^{40}K a naturally occurring radionuclide and gamma activity of any other nearby gamma emitters. A graded shield for a large volume (higher efficiency), high resolution detector system

helps in reducing the background contribution significantly.

The graded shield around a vertical 80 cc HPGe detector at Radiochemistry Division consists of concentric cylinders of 6 mm. thick aluminum, 6 mm. thick brass housed in an outer most cylinder made up from 5 cm. thick lead rings. The shielding at the top also had the same gradation. A door is provided for inserting or taking out the samples on the cylindrical side. The alkathene covered detector had been separated from the sample by 2 mm thick Perspex sheet so that chances of detector getting contaminated are minimized. The detector having FWHM of 1.8 keV at 1332 keV, was connected to 4 K channel analyzer through a spectroscopy amplifier and the background measurements were carried our repeatedly for 20 to 60 k seconds duration. Table 1 gives the performance of this system along with that of a systematically shielded 100 cc Ge(Li) detector system recommended by IAEA.

Estimation of Fission Products Activities in Grass Samples

After the Chernobyl accident on April 26, 1986, samples of grass and soil from different European countries were collected, dried and supplied by IAEA to the participating laboratories as part of an inter-comparison exercise. The long lived fission products, like ^{134}Cs, ^{137}Cs, ^{106}Ru-Rh, ^{90}Sr and ^{144}Ce were expected to be present apart from ^{40}K, ^{238}U and ^{232}Th in the samples received after 415 days.

The dried and powdered grass samples received from IAEA were present into 50 mm. dia. discs using a pneumatic die system at a pressure of

Table 2 - Concentration of radionuclide (in Bq/Kg) in the sample as on 26/05/86.
(The figures in the brackets are the average concentration levels reported by IAEA.

Sample No. (Country)	^{137}Cs	^{134}Cs	^{106}Ru	^{238}U	^{232}Th
9-B (Hungary)	2420 ± 220 (2295 ± 255)	1323 ± 30 (1191 ± 137)	403 ± 110 ———	——— ———	——— ———
G-13/9 (Italy)	87.5 ± 3.2 (95.4 ± 5.0)	41.4 ± 2.6 (34.6 ± 3.0)	——— ———	20 ± 15 (9.3 ± 7.5)	30 ± 20 (17.5 ± 10.5)

about 300 psi. The thickness of the discs varied from 5 to 7 mm, with weights in the range of 15 to 25 gms. These discs were kept in a specially designed perspex holder to maintain sample integrity.

To obtain the efficiency as a function of gamma ray energy, inactive dry powdered grass samples were prepared in identical fashion. Standard activities of a ^{152}Eu and ^{134}Cs were uniformly spread on three thin discs, which together had same thickness as that of the samples, were put in one sample holder. Three such standard samples were prepared for efficiency calibration.

The sample holder was placed in front of the HPGe detector in a fixed and closest geometry during counting. Each sample and all the three standards were counted at least five times, the counting times varying from 25 to 40 k sec. The background was measured in between the counting for durations of 20 to 60 k sec.

The gamma spectra of all the samples were analysed to obtain the Compton background subtracted peak areas for ^{106}Ru, ^{106}Rh, ^{134}Cs, ^{137}Cs, ^{232}Th and ^{238}U. The concentration of radionuclides in these samples was calculated using equation (1).

Under the experimental conditions used, the detection limits (MDC) for the radionuclides were of the order 2 to 5 Bq/Kg for ^{137}Cs, ^{134}Cs, ^{232}Th and ^{232}U

for a sample size of 25 grams and a counting time of 40 k sec. The systematic errors such as counting efficiency and branching intensities are of the order of 10% and 3% respectively. The ^{134}Cs/^{137}Cs is known to be directly related to the burn-up. The samples near the accident site were reported to have this ratio as 0.52. The average ratio of Cs activities in the grass samples collected from different European countries and supplied by IAEA was found to be 0.53 ± 0.3, indicating that the source of contamination for these samples is no other than Chernobyl incidence. Table 2 provides the analysis results for two typical samples.

It must be emphasized here that the gamma spectrometric method is capable of estimating the concentration of many short lived radionuclides in the environmental samples provided the samples can be analysed immediately after the release. Some of the participating laboratories which received the samples within a month of the Chernobyl incidence have indeed assayed many short lived and long lived radionuclides in the grass, mat and soil samples.

References

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