Chapter II

Experimental Techniques 
&
Methods
2.1. Introduction:

The focus of the present studies is to understand the influence of LMCA and HA on complexation and sorption of actinides and lanthanides. The complexation studies entail the measurement of the stoichiometry of the complexes and their stability constants while sorption studies deal with $K_D$ determination followed by spectroscopic characterization and SCM. In the present chapter, brief description of the methodology of sample and radiotracer preparation, their characterization and assay by different techniques viz., XRD, BET surface area analysis, zeta potential measurement, UV-Visible Spectroscopy, ICP-AES, TOC content, TRFS, Radiometry and the data analysis has been provided. In addition, aqueous speciation of radionuclides, linear additive and SCM used to model sorption phenomenon have been discussed in detail.

2.2. Preparation and Purification of Radiotracers:

The sorption studies on metal ions reported in the present thesis were carried out with radiotracers. Procurement, preparation as well as purification of various radiotracers are as follows:

2.2.1. Neptunium tracer:

$^{239}$Np, the short lived (2.35 days) $\beta/\gamma$-emitting isotope of neptunium was used as the tracer for neptunium in sorption studies. 15 mg of uranium (as $\text{U}_3\text{O}_8$) was irradiated in APSARA reactor at BARC having a neutron flux of $5 \times 10^{11}$ n/cm$^2$/s for 2 hours. After the irradiation, the uranium oxide was dissolved in 8 M HCl and the solution loaded on to a Dowex 1 X 8 anion exchange column of 3 mm diameter and 50 mm length. The column was washed with 8M HCl till all the fission products were washed from the column, which was monitored by gamma counting of the washings.
using HPGe detector (Eurysis Measures, France) coupled to a 4K MCA. Subsequently neptunium was eluted with 2 mL mixture of 4 M HCl and 0.05 M HF. The radiochemical purity of $^{239}$Np was ascertained by counting the eluted fraction on HPGe. The solution was evaporated to dryness and then evaporated with 1M HClO$_4$ three times and finally dissolved in 0.1 M NaClO$_4$ solution to prepare $10^{-11}$ M stock solution having pH ~ 6.

2.2.2. Uranium tracer:

$^{233}$U tracer ($t_{1/2} = 1.59 \times 10^5$ years) was produced by the irradiation of $^{232}$Th followed by its purification (Srinivasan et al., 1972). Purification of $^{233}$U from its daughter products and Thorium was carried out from 6 M HCl using anion exchange procedure (Rattan et al., 1981). Uranium in 6 M HCl solution forms anionic complex which is held on the column, whereas thorium and daughter products are not retained on the column. The column was washed with excess of 6 M HCl to remove any adsorbed impurities. Finally, the loaded uranium was eluted with 0.01 M HNO$_3$. The radiochemical purity of $^{233}$U tracer was ensured by alpha spectrometry. The eluted fraction was evaporated to dryness thrice and the residue obtained was dissolved in ~ 0.01 M HClO$_4$. The concentration of uranium in the $^{233}$U stock solution thus obtained was $8.95 \times 10^{-5}$ M.

2.2.3. Curium tracer:

Existing stock of $^{244}$Cm at Radiochemistry Division, BARC was used as a tracer for curium. The alpha spectrometric assay of the curium solution showed it to be 99% $^{244}$Cm and 1% $^{245}$Cm. The curium concentration in stock solution was $2.2 \times 10^{-8}$ M.
2.2.4. Europium tracer:

Natural Eu$_2$O$_3$ (10 mg) sealed in quartz was irradiated in Dhruva reactor at BARC having a neutron flux of 5 X $10^{13}$ n/cm$^2$/s for 7 days. After cooling period of two days, the irradiated Eu$_2$O$_3$ was dissolved in conc HClO$_4$ and finally diluted to pH 2 with water to prepare the $^{152,154}$ Eu stock solution. The concentration of Eu(III) in the stock solution was $2 \times 10^{-4}$ M.

2.3. Synthesis of hematite:

Hematite was synthesized by neutralization of aqueous ferric chloride (AR grade, 0.5 M) solution with sodium hydroxide solution (AR grade, 0.5 M) followed by thermostating the precipitate at 800$^\circ$C to transform it into granular precipitate in an air oven. It was filtered, washed repeatedly with distilled water to remove counter ions and oven dried. The dried precipitate was further heated at 300$^\circ$C for one hour to form crystalline hematite. The crystalline powder was ground to sub-micron size particles in a planetary ball mill (Ms FRITSCH, Germany).

2.4. Radiometric Techniques:

Alpha emitting radionuclides e.g. $^{244}$Cm and $^{233}$U were assayed in the sorption experiments by liquid scintillation counting whereas NaI(Tl) scintillation counter and HPGe detector were used for the estimation and radionuclide purity of gamma emitting radionuclides respectively.

2.4.1. Liquid Scintillation Counter:

For quantitative analysis of alpha emitters, liquid scintillation counters are most widely used. The main advantage of these detectors is nearly 100% detection efficiency which allows assay of as low as few Bq of alpha activity with good precision. A scintillator is a material that emits luminescence in a suitable wavelength
region when ionizing radiation interacts with it. Interaction of the charged particles (alpha particles) with the scintillator results in emission of photons, which are converted into a voltage signal using a PMT. The height of the voltage signal is a measure of the energy of α particle while the number of pulses gives the activity of the source. In cases, where the scintillator emits photons in UV region, a wavelength shifter is added to the scintillator in order to shift the wavelength of the emitted photons to visible region which is subsequently collected in the PMT since photomultiplier tubes (PMTs) are compatible with visible light. The liquid scintillation counters provide data on the gross alpha activity as it cannot distinguish between alpha energies and therefore it cannot be used for alpha spectrometry. Many organic compounds are versatile scintillators for radiation measurements (Horrocks and Peng, 1971). The liquid scintillation cocktail comprises of a solvent like dioxane or toluene, a scintillator like PPO (2,5-diphenyl oxazole) and a wavelength shifter such as POPOP (1,4-bis-2-(5-phenyl oxazolyl)-benzene). The solvent is the main stopping medium for radiation and must be chosen so as to provide the efficient energy transfer to the scintillating solute. In the present work, the concentration of the radiotracers was kept low so as to mimic natural conditions and hence generally large volume of aqueous aliquots (1 mL) was added to scintillators. Thus di-isopropyl naphthalene based scintillators which satisfied all the requirements were employed for alpha counting. Each sample was counted for sufficient time so as to get more than 10,000 counts to minimize the statistical counting error.

2.4.2. NaI(Tl) Scintillation Counter:

Sodium iodide activated with 0.1-0.2% of thallium, NaI(Tl), is by far the most widely used inorganic scintillator for the assay of gamma emitting radionuclides. Salient features of these detectors are the low cost, ease of operation and ruggedness
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(The band gap in NaI crystal is of the order of 5-6 eV. When a charged particle (or gamma ray) falls on the detector its energy is used up either for excitation of electrons from the valence band to conduction band or for the ionization of atom. Introduction of thallium in the NaI(Tl) not only shifts the wavelength to higher value by creating intermediate levels in conduction bands but also increases the fluorescence yield of the detector. The energy resolution of NaI(Tl) detector is about 7% at 662 keV.

In the present work, a 3” x 3” well type NaI(Tl) detector coupled with a multichannel analyzer has been used for gamma counting. Nearly 100% detection efficiency for moderate energy photons in a well type NaI(Tl) detector offers great advantages for counting of low activity samples. A suitable aliquot (1 mL) of the desired analyte solution was taken in glass counting tubes which was then placed in the cavity of detector coupled with PMT and associated electronics. Each sample was counted for sufficient time so as to get more than 10,000 counts to reduce the statistical error in counting.

2.4.3. HPGe:

In the present work, HPGe detector coupled with multichannel analyzer was employed for gamma spectroscopy to check the radiochemical purity of the radionuclides. The HPGe detector is made up of exceptionally pure germanium in which the impurity level is around \(10^{10}\) atoms/cm\(^3\) or less. This is referred to as high purity germanium which approaches the theoretical pure semiconductor. HPGe is the most widely used semiconductor detector for gamma spectrometry and can be called as the workhorse of gamma ray spectroscopy. The high energy resolution (typically 1.9 keV at 1332 keV) is the key feature of this detector due to low band gap (0.7 eV). The great advantage of HPGe detector is that it can be stored at room temperature.
(Knoll, 2000). However, while operating it has to be cooled to liquid nitrogen temperature. In present work radiochemical purity of $^{239}$Np and $^{152}$Eu was ascertained by using HPGe.

2.5. XRD:

XRD is one of the non-destructive, fast and most widely used techniques to characterize single crystal, polycrystalline and amorphous materials. The ease of sample preparation and highly-accurate determination of d-spacing calculations has made XRD, a versatile tool in the field of material chemistry. In crystalline materials, due to the presence of long range periodicity, the XRD patterns are in the form of sharp peaks.

The underlying principle of XRD is based on scattering of X-rays by a crystal consisting of well-defined array of atoms, ions and molecules. Since parallel arrays of atoms of the crystal lattice are equivalent to the parallel lines of the diffraction grating, therefore inter-planar spacing could be successfully determined from the separations of bright fringes of the diffraction pattern. The wavelength of X-rays (0.5 to 2 Å) has same magnitude as interplanar spacings in the crystal lattice and therefore crystal planes act as diffraction gratings for impinging X-ray radiation. X-rays interact with the electron cloud of the atoms which act as scattering centers and the scattered X-rays from two scattering centers may undergo constructive or destructive interference. Interaction of X-rays reflected by a set of parallel planes lead to constructive interference only at a particular angle according to Bragg’s Law, given by equation (2.1), which results in sharp peaks in XRD pattern and are characteristic of a particular material.

\[ n\lambda = 2d \sin \theta \]  

(2.1)

where,
\( n \) is the order of diffraction
\( \lambda \) is the wavelength of X-rays,
\( \theta \) is the glancing angle (called as Bragg's angle),
\( d \) is the inter-planar separation

In general, in most of the diffractometers Cu K\( \alpha \) is used as the X-ray source and a proportional counter (Argon filled) as the detector. In present work, XRD (Stoe \( \theta-\theta \) diffractometer, Germany) was used to characterize mineral oxide hematite.

2.6. BET Surface Area Analyser:

BET surface area analysis is an important analysis technique for the measurement of the surface area of a material. This technique is based on BET theory, given by Brunauer-Emmett-Teller, which explains the physical adsorption of gas molecules on a solid surface.

The BET theory explains multilayer adsorption by taking into consideration following hypotheses: (a) gas molecules are physically adsorb on a solid in infinite layers at saturation pressure; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed by (2.2):

\[
\frac{1}{v \left( \frac{p}{p_0} \right)^{-1}} = \frac{c^{-1} v_{mc}}{v} \left( \frac{p}{p_0} \right) + \frac{1}{v_m c} 
\]  

(2.2)

\( p \) and \( p_0 \) are the equilibrium and the saturation pressure of adsorbate at the temperature of adsorption, \( v \) is the volume of adsorbed gas, and \( v_m \) is the volume of adsorbed gas for monolayer formation. \( c \) is the BET constant, which is expressed by (2.3):

\[
c = \exp \left( \frac{E_1 - E_i}{RT} \right)
\]

(2.3)
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$E_1$ is the heat of adsorption for the first layer, and $E_L$ is that for the second and higher layers and is equal to the heat of liquifaction.

Equation (2.2) is a BET adsorption isotherm and can be plotted as a straight line with $1/v[(p_0/p)-1]$ on the y-axis and $(p_0/p)$ on the x-axis. The value of the slope and the intercept are used to calculate the monolayer adsorbed gas quantity $v_m$ and the BET constant $c$.

The surface area of the material can be evaluated by use of following equation:

$$S = \frac{(v_mNs)}{V a}$$

(2.4)

where

$N$ : Avogadro's number,
$s$ : adsorption cross section of the adsorbing species,
$V$ : molar volume of adsorbate gas
$a$ : mass of adsorbent (in g)

In present work, surface area of mineral oxides was determined using BET surface area analyser (Sorptomatic 1990, CE Instruments, UK).

2.7. UV-Visible Spectrophotometry:

UV-Visible Spectrophotometry refers to absorption spectroscopy in the ultraviolet-visible spectral region. Spectrophotometry is one of the direct methods for determining concentration of the species as the spectra obtained are characteristic of particular species. The observed spectra thus provide information about the species formed which are helpful in both qualitative and quantitative estimations.

The principle of UV-Visible Spectrophotometry is based on the Lambert – Beer law according to which equal fractions of the incident light are absorbed by
successive layers of equal thickness and equal concentration of absorbing medium.

Mathematically, Lambert – Beer law is given by equation (2.5)

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon cl$$  \hspace{1cm} (2.5)

Where,

$I_0 = \text{intensity of light incident on the sample}$

$I = \text{intensity of transmitted light}$

$A = \text{absorbance}$

$\varepsilon = \text{Molar extinction coefficient which is the characteristic of species}$

$c = \text{concentration of species}$

$l = \text{path length}$

In this technique, absorption of electromagnetic radiation results in transition from the ground state to the excited state. The wavelength, at which maximum absorption for species is observed, $(\lambda_{\text{max}})$, is used for its spectroscopic analysis. The absorption spectrum is a reflection of structure of a species and therefore absorption spectra provide information about the functional groups as well as oxidation state of metal ion in a particular species. A schematic diagram of a standard spectrophotometer is given in figure 2.1.

In the present case, UV-Visible absorption spectra of the HA samples were recorded, using a Jasco V-350 UV/Vis spectrophotometer at ambient conditions, in order to determine the fraction of HA sorbed on hematite. The equipment uses deuterium lamp and halogen lamp as source of radiation for ultraviolet and visible region respectively. A PMT is used for detection of transmitted photons. The instrument has a resolution of 1 nm with wavelength accuracy of $\pm 0.5$ nm.
2.8. ICP-AES:

ICP-AES is one of the most common techniques for elemental analysis. Its high specificity, multi-element capability and good detection limits make this technique suitable for a wide variety of applications. A plasma source is used for dissociation of the sample into its constituent atoms or ions, and their subsequent excitation to a higher energy level. They return to their ground state by emitting photons of a particular wavelength which is characteristic of the element present. This light is recorded by an optical spectrometer. When calibrated against standards the technique provides a quantitative analysis of the original sample.

A JY-50P poly scan instrument with axial ICP and operated at 40.68 MHz radio frequency (r.f) with 1.0 kW forward output r.f. power served as the spectral excitation source. The instrument known as “Panorama” model has a unique facility for simultaneous and sequential operation in the same spectrometer assembly. Thus, the spectrometer has a polychromator covering 35 elements and is also able to function as a sequential unit over a spectral range of ± 2.2 nm around each channel. The block diagram of ICP-AES is given in figure 2.

In present work, ICP-AES has been used for the determination of dissolved silica.
2.9. Determination of Zeta potential:

The ionization of surface groups, lattice imperfection and specific ion adsorption leads to development of a surface charge at the particle surface which in turn affects the distribution of ions in the surrounding interfacial region and hence increase in concentration of counter ions close to the surface which ultimately leads to the formation of electric double layer around each particle. There exists a notional boundary within the diffuse layer inside which the ions and particles form a stable entity and move along with the particle, but any ions beyond the boundary do not travel with the particle. This boundary is termed as shear plane and the potential at this plane is known as the Zeta potential as shown in figure 2.3.

The stability of the colloidal system can be ascertained in terms of magnitude of the zeta potential. Large negative or positive zeta potential values (≥ ± 30 mV) of colloidal system generate repulsion among particles and thus avoid tendency of flocculation. Such systems are termed as stable suspensions. In contrast low zeta potential values (≤ ± 30 mV) offer low electrostatic repulsion which results in flocculation and these systems are called unstable suspensions. The point where zeta potential becomes zero is called the isoelectric point or pH \( \text{pzc} \) and is one of the very important parameters used for characterizing the colloidal systems.
The zeta potential measurement involves determination of electrophoretic mobility which is defined as the velocity of a particle in an electric field. The charged particles suspended in the electrolyte are attracted towards the electrode of opposite charge on application of electric field but their movement is opposed by viscous forces acting on them. When equilibrium is attained between these two opposing forces, the particles move with constant velocity. The velocity i.e. electrophoretic mobility of the particle \((U_E)\) is dependent on the strength of electric field, the dielectric constant \((\varepsilon)\) and the viscosity \((\eta)\) of the medium and the Zeta potential \((z)\). The electrophoretic mobility and zeta potential is related by Henry equation (2.6)

\[
U_E = \frac{2\varepsilon f(Ka)}{3\eta}
\]  

\((2.6)\)

\(f(Ka)\) is known as Henry’s function and generally have two values either 1.5 or 1.0.

Figure 2.3 Schematic showing Electrical double layer and Zeta potential
This velocity is measured using the technique of the Laser Doppler Velocimetry. The frequency shift or phase shift of an incident laser beam caused by these moving particles is measured as the particle mobility, and from this mobility zeta potential is determined using equation (2.6). In present studies the zeta potential determination of hematite and silica were carried out using Malvern, Zetasizer Nano ZS.

2.10 TOC Analyser:

TOC is the amount of carbon bound in an organic compound. A typical analysis for TOC measures both the total carbon present as well as the so called "inorganic carbon" (IC), the latter representing the content of dissolved carbon dioxide and carbonate salts. Subtraction of IC from the total carbon yields TOC. But nowadays, direct determination of TOC can be made using photocatalytic oxidation followed by infra red detection.

Introduction of sample directly into the photocatalytic reactor allows direct mixing with the titanium dioxide (catalyst) slurry in the presence of a near-UV light source (300-400 nm). There is continuous circulation of air in a closed loop system and the reactor provides the necessary oxygen. Under these conditions any bound organic carbon present in the sample is quickly oxidized.

\[ 4C_xH_y + (4x + y)O_2 \rightarrow 4xCDO_2(g) + 2y H_2O \]  \hspace{1cm} (2.7)

The carbon dioxide that is formed during this reaction is passed through a condenser and then circulated through the closed loop system. A dual wavelength Non-Dispersive Infra-Red detector measures the increase in carbon dioxide resulting
from the oxidation. The block diagram of TOC analyser is shown in Figure 2.4. For quantitative analysis of TOC, benzoic acid is used as a standard.

In present studies, Anatoc analyzer (SGE, Australia), with detection limit 0.5 ppm carbon, has been employed to determine the sorption of HIBA and citric acid on silica.

Figure 2.4 Schematic of TOC analyser

2.11. TRFS:

For a comprehensive understanding of the interaction mechanisms between trivalent lanthanides/actinides and the chosen minerals and complexing ligands, TRFS have been employed. TRFS is one of the most sensitive, non-invasive and widely used spectroscopic techniques for speciation studies. The technique has triple advantage of (i) characteristic excitation wavelength, (ii) characteristic emission wavelength and (iii) characteristic lifetime which helps in accurate assignment of the complex stoichiometry and structure in both sorption as well as complexation studies.
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(Plancque et al., 2003). The fluorescence emission spectra are characteristic of particular species and the selective excitation helps in reduction of interferences from others species. Thus spectral characteristics and lifetime of species provide information about the important properties like oxidation states of metal ions, coordination numbers, and covalence. Due to the above mentioned advantages, TRFS has been used extensively for speciation studies.

2.11.1. Principle of TRFS:

Photoluminescence is a process in which a substance absorbs photons (electromagnetic radiation) and then emits its characteristic luminescence. Quantum mechanically, this can be described as an excitation to a higher energy state and then return to a lower energy state accompanied by the emission of a photon. The various deexcitation pathways of an excited molecule can be described with the help of Jablonski diagram as shown in figure 2.5. $S_0$, $S_1$, and $S_2$, depict the singlet ground, first, and second electronic states respectively. The vertical lines are used to depict transitions between different electronic states. The light absorption is instantaneous in nature ($10^{-15}$ s). Following light absorption, several processes usually occur. A fluorophore is usually excited to some higher vibrational level of either $S_1$ or $S_2$ and rapidly relax to the lowest vibrational level of $S_1$. This process is called internal conversion and generally occurs within $10^{-12}$ s or less. When the relaxation occurs between an excited state and the ground state of same spin multiplicity ($\Delta S = 0$) the luminescence process is referred to as fluorescence. Thus, fluorescence emission generally results from a thermally equilibrated excited state, that is, the lowest energy vibrational state of $S_1$. Although the fluorescence is a fast process, some of the original energy is dissipated so that the emitted light photons are of lower energy than those absorbed. The generated photon in this case is said to be red shifted as the result
of loss of energy in internal conversion. Molecules in the $S_1$ state can also undergo a spin conversion to the first triplet state $T_1$ which is termed as intersystem crossing. Emission from $T_1$ is termed phosphorescence, and is generally shifted to longer wavelengths (lower energy) relative to the fluorescence. Transition from $T_1$ to the singlet ground state is quantum mechanically forbidden, which result in a slow process of radiative transition back to the singlet ground state, sometimes lasting even minutes or hours (Lakowicz, 2006). Typically, this is correlated with the relaxation time that is longer for phosphorescence than for fluorescence.

**Figure 2.5** Jablonski diagram depicting photo physical processes

Some f-elements relax through intense luminescence emission in aqueous media. Some actinide and lanthanide fluorophores are Am(III), Cm(III), Bk(III), Cf(III), Pa(IV), U(VI), Eu(III), Gd(III), and Tb(III). The characteristic optical spectra of these inner transition elements originate from f-f transitions, taking place between
the partly filled 4f (lanthanides) and 5f (actinides) energy levels (Carnall, 1979). The
f-f transitions are sensitive to changes in the ligand field, thus, making TRFS an
extremely useful tool to probe the complex speciation of these elements.

2.11.2. Instrumentation:

The present TRFS studies were carried out using an Edinburgh 920 series
spectrometer which works on the principle of TCSPC. The spectrometer is equipped
with a Xe flash lamp and a couple of M 300 monochromators providing resolution of
~1 nm.

2.11.2.1. Xenon flash lamp:

A Xenon flash lamp is an electric arc lamp designed to produce extremely
intense, incoherent, full-spectrum white light for very short durations. Flash lamp
comprises a hermetically sealed glass tube, in which noble gas xenon is filled with
electrodes at either end to carry electrical current. The electrodes of the lamp are
usually connected to a capacitor, which is charged to a relatively high voltage
(generally between 250 and 5000 volts). The gas, owing to its inert nature, exhibits
extremely high resistance, and the lamp does not conduct electricity until the gas is
ionized. On ionization, a spark forms between the electrodes, allowing the capacitor
to discharge. The sudden surge of electric current quickly heats the gas to a plasma
state, where electrical resistance becomes very low, and a high voltage pulse is
generated to produce the light.

2.11.2.2. Monochromator:

The dispersion of polychromatic or white light into the various colors or
wavelengths is achieved by using monochromators. In most spectrofluorimeters, the
dispersion into light of specific wavelength is attained by using diffraction gratings, an optical component with a periodic structure that splits and diffracts light into several beams travelling in different directions. The directions of these beams depend on the spacing of the grating and the wavelength of the light. The relationship between the grating spacing \( d \), the angles of the incident \( \theta_i \) and diffracted beams \( \theta_r \) of light is known as the grating equation which is given in equation (2.11)

\[
m \lambda = d \left( \sin \theta_i \pm \sin \theta_r \right)
\]  

where \( m \) is the order of diffraction and \( \lambda \) is the wavelength.

M300 monochromator, dispersive element in the instrument used for present studies, is a high quality general purpose grating monochromators designed for use in the UV, visible and infra-red spectral regions. All the gratings are kinematically mounted so that calibration is not lost when gratings are changed. The use of an 1800 lines/mm of 69 mm x 69 mm grating in the visible region results in a higher resolution and light gathering power.

2.11.2.3. TCSPC

TCSPC technique is a digital counting technique where the photons, that are time correlated in relation to an excitation light pulse, are counted. The sample is excited with light pulse, resulting in the waveform, as shown in the figure 2.6, which excite many fluorophores and numerous photons are observed. However, the conditions for TCSPC are so adjusted that less than one photon is detected per laser pulse. In fact, the typical detection rate is 1 photon per 100 excitation pulses. The time difference between the excitation pulse and the observed photon is measured and stored in a histogram which represents the waveform of decay provided less than one photon per 100 excitation pulse is detected. The excitation pulse, in addition to sample excitation, triggers the start PMT which sends an analog signal to CFD that
generates a logic signal which represents the accurate arrival time of the pulse. This signal is passed to TAC as a start signal, which generates a linear voltage ramp with respect to time. As soon as the first fluorescence photon is observed, stop PMT detects the photon and the arrival time of the signal is accurately determined using a CFD, which sends a signal to stop the voltage ramp. The voltage contained in TAC is proportional to the time delay (t) between the excitation and emission signals.

**Figure 2.6** Principle of TCSPC depicting excitation pulse and decay profile

*(Lakowicz, 2006)*

The sample is repetitively excited and a probability histogram relating the time difference between an excitation pulse (Start) and the observation of the first fluorescence photon (Stop) is obtained. The time of arrival of photon must be defined precisely and accurately in TCSPC. This precise timing information is achieved by CFD. The schematic diagram of TCSPC set up used for fluorescence investigations is shown in figure 2.7.
2.11.2.4. CFD:

The analog signal from PMT corresponding to individual photon detection, have a significant spread in pulse height which means that timing based on amplitude threshold will result in considerable jitter as shown in figure 2.8.

![Figure 2.7 Block diagram of TCSPC set up for fluorescence experiments](image)

**Figure 2.7** Block diagram of TCSPC set up for fluorescence experiments

![Figure 2.8 Constant fraction discrimination in TCSPC. (a): Timing error due to pulse height variations (b): Operation of a CFD (Lakowicz, 2006)](image)

**Figure 2.8** Constant fraction discrimination in TCSPC. (a): Timing error due to pulse height variations (b): Operation of a CFD *(Lakowicz, 2006)*

The accurate timing information about a photon is obtained with the help of CFD in which input signal is split into two parts, one part is delayed by about half the
pulse width and the other part of the signal is inverted. On summing of these two parts, the zero crossing point is independent of the pulse height which accurately determines the arrival time of the signal (Lakowicz, 2006).

Figure 2.9 shows the TRFS setup used for present work.

2.12.3. Data treatment and Error analysis:

Decay curve analysis is a very vital aspect of the TCSPC technique. In reality δ-pulse excitation is impossible as all excitation sources have their finite pulse width and therefore measured decay is the convolution of the true decay and the excitation pulse profile. Therefore analysis of decay curve involves following steps:

(a) Removal of distortion introduced by excitation pulse and extraction of true sample decay profile

(b) Evaluation of parameters to ascertain goodness of fit
The first step is carried out using deconvolution procedure. The observed fluorescence decay curve is convolution of excitation pulse and decay profile of sample. Mathematically, the observed decay curve, \( F(t) \), is given by equation (2.12)

\[
F(t) = \int_0^t I(t - t')D(t')dt
\]  

(2.12)

where \( D(t') \) represents sample decay profile while \( I(t) \) represents instrument response function i.e lamp profile which is measured by replacing the sample by scattering solution and resetting the emission monochromators to the excitation monochromators.

In our analysis program, reconvolution is employed which involves convoluting a theoretical model, that is assumed to represent the sample decay, with an instrument response function and the resultant convolution integral is compared with observed decay curve. However, it is possible to do exponential fitting without reconvolution analysis by excluding instrument response function. Thus, sample decay curve, \( D(t) \), can be represented as

\[
D(t) = \sum_{i=1}^n B_i \exp \left( -\frac{t}{\tau_i} \right)
\]  

(2.13)

where \( n \) is the number of species in the decay curve and \( \tau \) represents the lifetime of each species and is defined as the average time the molecule spends in the excited state prior to return to the ground state.

Nonlinear least square fitting is used to compare the theoretical function and measured data. The goal of least squares is to test whether a given mathematical model is consistent with the data, and to determine the parameter values for that model which provide best match between observed and calculated decay which is achieved by minimization of the goodness-of-fit parameters. Statistical parameters which are used to judge the goodness of fit are described in brief.
(a) Chi square value ($\chi^2$):

$\chi^2$ is defined as follows:

$$\chi^2 = \sum_t \left[ \frac{D(t) - F(t)}{\sigma(t)} \right]^2$$  \hspace{1cm} (2.14)

where $D(t)$ is raw fluorescence data, $F(t)$ is the fitting function and $\sigma(t)$ is the statistical uncertainty of point $D(t)$. The aim is to adjust the fitting parameters such that lowest value of $\chi^2$ is obtained. Thus, if the fitting function represents the observed decay accurately then the ratio of actual deviation to expected deviation will be equal to number of data points, $N$. It is not convenient to interpret the values of $\chi^2$ as it is dependent on number of data points. Therefore, reduced $\chi^2$ is used which is obtained by normalizing $\chi^2$ by degree of freedom.

$$\chi^2_R = \frac{\chi^2}{(n-p)}$$  \hspace{1cm} (2.15)

where $n$ is the number of data points, $p$ is the number of floating parameters, and $n - p$ is the number of degrees of freedom. For TCSPC the number of data points is typically much larger than the number of parameters so that $(n - p)$ is approximately equal to $n$. Thus,

$$\chi^2_R = 1$$  \hspace{1cm} (2.16)

(b) Weighted Residuals:

Weighted Residuals are very important means of determining the goodness of fit. The weighted residuals are the difference between the fitted function and the measured data, normalized by data uncertainty. Thus,

$$R(t) = \frac{y(t) - F(t)}{\sigma^2(t)}$$  \hspace{1cm} (2.17)

Hence

$$X^2 = \sum_t R((t))$$  \hspace{1cm} (2.18)
For a good fit, weighted residuals should be randomly distributed around zero among the data channels.

2.12. $K_D$ determination of radionuclides:

Sorption plays an important role in reducing the mobility of radionuclides in natural systems. Initial research for modeling performance assessment related to nuclear waste repositories dealt with determination of solid/liquid $K_D$ which is measured as the concentration ratio of radionuclides on solid and in aqueous phase under well defined set of experimental conditions of temperature, pressure, Eh, pH, ionic strength and solid/solution ratio. Thus, the $K_D$ is expressed as

$$K_D = \frac{C_s}{C_l}$$

(2.8)

where $C_s$ is the concentration of radionuclide per gram of solid and $C_l$ is the concentration of radionuclide per mL of aqueous phase. Since the speciation of radionuclides is quite complex, specially for lanthanides and actinides, many species for a particular radionuclide can exist simultaneously for given set of experimental parameters but $K_D$ represents the gross distribution of radionuclide at solid/solution interface without considering their speciation.

Another parameter, which is commonly used in surface chemistry to evaluate the distribution of radionuclide at solid/solution interface, is % sorption which is defined as

$$\% \text{ sorption} = \left( \frac{C_i - C_f}{C_i} \right) \times 100$$

(2.9)

where $C_i$ and $C_f$ are the initial and final concentration, after sorption on solid surface, of radionuclides in aqueous phase. The % sorption and $K_D$ are related by following equation:
\[
\% \text{sorption} = \frac{K_d}{K_{d+1}} \times 100
\]  \hspace{1cm} (2.10)

Generally, batch sorption method is used for \(K_D\) determination. The design of the batch sorption experiments employed for present studies is discussed below.

2.12.1. Experimental Details:

Batch sorption experiments were carried out in 50 mL Oak Ridge polypropylene tubes. The mineral oxides, after characterization for surface properties, were suspended in aqueous phase of fixed ionic strength in fixed solid to liquid ratio for 12 to 24 hours. \(\text{NaClO}_4\) was used to maintain the ionic strength owing to least complexing tendency of the perchlorate ion. Subsequently appropriate quantity of radionuclide was added in order to achieve desired radionuclide concentration. The control, prepared in 0.1 M \(\text{HClO}_4\) but without mineral oxide, was taken for each of the sorption experiment in order to determine the initial concentration of radionuclide (Ci). Thereafter, pH of the suspensions was adjusted in the range 2-10 using dil \(\text{NaOH}\) and dil \(\text{HClO}_4\). While adjusting the pH, drop wise addition of acid/base was done so as to avoid local changes in radionuclide speciation. The pH adjustment was followed by equilibration of suspensions for a time period which was fixed based on kinetics experiments. Post equilibration, the pH of the suspensions was checked, recorded and suspensions were centrifuged at appropriate centrifuge speed for appropriate time to separate the phases. A suitable aliquot (1 mL in most of the cases) of supernatant was taken for determining the concentration of radionuclide in supernatant (Cf) after equilibration. Once Ci and Cf were known, \% sorption at varying pH was determined for radionuclides. In ternary systems, where the effect of complexing ions on radionuclide sorption is investigated, suspensions were equilibrated with complexing anions, in similar manner as mentioned above, prior to radionuclide addition. It is
worth mentioning that pH of suspensions were readjusted after radionuclide addition so that radionuclide and complexing ion equilibrate at same pH. Similar methodology was adopted for ternary systems in which radionuclide addition was preceded by addition of complexing anion.

2.12. Error determination on sorption data:

In order to quantify the error on sorption data, it is essential to identify the sources of error. In present work radionuclides investigated are mainly lanthanides and actinides which undergo extensive hydrolysis. Therefore it is imperative to their check sorption on walls of polypropylene containers. The wall sorption was estimated by removal of suspensions from the polypropylene container and subsequently tube was rinsed with distill water followed by addition of 1.0 M HNO$_3$ in same quantity as that of aqueous phase in sorption experiments. After 24 hours, the solution was assayed so as to estimate the leached radionuclide from walls of the container. The wall sorption was quantified as the ratio of concentration of radionuclide leached into HNO$_3$ to the initial concentration of radionuclide in the sorption experiments. Negligible wall sorption was obtained in systems investigated in present work.

The other errors viz., random errors, systematic errors were taken into account by performing duplicate measurements and calculating standard deviation. Since duplicate measurements for entire range of pH is difficult, statistical error on radioactive counting was considered while calculating the error on sorption.

2.13. Modeling of sorption data:

Initially, K$_D$ approach was commonly used for modeling adsorption on solid surfaces and migration of radionuclides in geosphere. The severe weakness of the K$_D$ approach is that all physico-chemical interactions taking place at the solid solution
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interface are represented by purely phenomenological parameter. Such \( K_D \) tend to exhibit large uncertainties when inter- or extra polation to other system is required. Surface reaction mechanisms and changes in chemical environment are also neglected in \( K_D \) approach. In order to have the fundamental understanding of the type of interaction taking place at solid/solution interface and development of efficient thermodynamic sorption database, sorption models which can overcome the above mentioned short comings are required. In present work, two modeling approaches namely LAM and SCM are used, which are discussed below:

2.13.1. LAM:

The LAM, a mathematical model, is used for predict the sorption of metals onto surfaces in the presence of HA. In ternary system, metal cations, HA and the solid or colloid surface coexist. The different interactions of ternary system are shown in figure 2.10.

LAM is based on the series of assumptions which are given below (Samadfam et al., 1998,2000; Sakuragi et al., 2004; Christl and Kretzschma,. 2001):

a) \( K_D \) for the ternary system is a combination of the distribution coefficients of the separate binary interactions.

b) The individual sorption coefficients are independent of the metal concentration.

c) The sorption properties or characteristics of the mineral are not affected by the presence of HA.

d) Different molecular weight fractions of HA are neglected and sorption of HA is considered as a whole.
e) Affinity of metals for mineral-bound HA and for dissolved HA are considered identical.

f) The mass of mineral is much higher than the mass of mineral-bound HA.

g) Electrostatic interactions at the mineral-water interface are neglected.

\[
K_D = \frac{k_D^0 + \frac{V}{W} f_{HA} \beta [HA]}{1 + (1 - f_{HA}) \beta [HA]} \tag{2.19}
\]

where, \( \beta \) is metal-humate stability constant, \( K_D^0 \) is the distribution coefficient for the binary metal-solid surface interaction, \( f_{HA} \) is the fraction of HA sorbed onto the surface, \( V \) and \( W \) are the volume of solution and weight of solid respectively and \( [HA] \) is the concentration of HA in solution.

2.13.2. SCM:

SCM are used to describe the equilibrium reactions that take place at the solid/solution interface. SCM enables treatment of sorption data by taking into consideration main basic processes defining overall sorption phenomenon. It considers sorption of ions at solid/solution interface similar to complexation in...
solution, and electrostatic effects at the surface-solution interface are addressed by theories describing the electrical double layer.

An accepted mechanism for oxide surfaces is to introduce the concept of amphoteric surface sites i.e. general hydrolysed species, ≡SOH. The pH dependent surface charge arises due to the protonation/deprotonation of the hydroxylated functional groups according to the following equations

\[ \equiv SOH + H^+ \leftrightarrow \equiv SOH_2^+ \quad (K_1) \]  
\[ \equiv SOH \leftrightarrow \equiv SO^- + H^+ \quad (K_2) \]

where \( K_1 \) and \( K_2 \) are the intrinsic equilibrium constants for the reactions 2.20 and 2.21 respectively. The mass law equations corresponding to the equations 2.20 and 2.21 are,

\[ K_1 = \frac{[SOH]^+}{[SOH][H^+]} \exp \left( \frac{F\psi}{RT} \right) \]  
\[ K_2 = \frac{[SO^-][H^+]}{[SOH]} \exp \left( -\frac{F\psi}{RT} \right) \]

where \([X]\) refers to the concentration of species X. The argument of the exponential term represents the Coulomb term that accounts for the change in electrostatic energy during the surface chemical reaction (Dzombak and Morel, 1990). \( R \) is the molar gas constant, \( T \) the absolute temperature (K), \( F \) is the Faraday constant and \( \psi \) represents the surface potential. In SCM, the adsorption on a surface is calculated as a function of the surface potential which cannot be determined directly. Therefore determination of surface charge density, \( \sigma \), is done which can be related to surface potential, \( \psi \). Several expressions have been proposed to relate \( \Psi \) to \( \sigma \), and based on these expressions; different SCMs have been proposed viz., CCM and DLM.
2.13.2.1. CCM:

The CCM was developed by Schindler and coworkers (Dzombak and Morel, 1990). It is applicable at high ionic strength or at very low surface potential values. It also assumes that all the surface complexes are inner-sphere complexes. The relationship between surface charge density ($\sigma_0$) and surface potential ($\psi_0$) (where 0 indicates the surface plane), in the CCM is given by the following equation:

$$\sigma_0 = \frac{CAS}{F} \psi_0$$  \hspace{1cm} (2.24)

where, C is the capacitance density (F/m²), A is the surface area (m²/g), S is the sorbent density (g/L). A diagram of the structure of the surface-solution interface for the CCM is shown in figure 2.11.

![Diagram of surface-solution interface for CCM](image)

**Figure 2.11** Conceptual representation of surface charge development in: A) DLM B) CCM (Hayes et al., 1991)

2.13.2.2. DLM:

The DLM was developed by Stumm and his co-workers (1970). The model assumes two planes for surface charge: a surface layer (plane 0) and diffuse layer of
counter ions (plane d). A diagram of the structure of the surface-solution interface for DLM is shown in figure 2.11. The relationship between surface charge and surface potential is described with the Gouy-Chapman theory which is based on following assumptions:

a) The ions in the solution are assumed to be point charges.
b) Correlations between the ions in the solution are not taken into account.
c) The surface charge is homogeneous.
d) The liquid is homogeneous and the dielectric constant $\varepsilon$ is not affected by the electric field from the surface.
e) The concentration of ions at any location in the electrical double layer is related to the bulk ion concentration by the Boltzmann distribution.

The relation between surface charge density ($\sigma$) and surface potential ($\psi$), based on above assumptions, can be derived as follows:

According to Gauss Law, the total electric flux coming out of a closed surface is equal to the charge enclosed divided by the permittivity as illustrated in equation (2.25)

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho(r)}{\varepsilon_0 \varepsilon_r}$$  \hspace{1cm} (2.25)

where $E$ is the electric field, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_r$ is the permittivity of medium and $\rho$ is the charge density. The electric field is differential of electric potential $\psi$.

$$\vec{\nabla} \cdot \psi(r) = \frac{\rho(r)}{E}$$ \hspace{1cm} (2.26)

Thus, on combining equation (2.25) and (2.26), we have

$$\vec{\nabla} \psi(r) = \frac{\rho(r)}{\varepsilon_0 \varepsilon_r}$$ \hspace{1cm} (2.27)
For one dimension, the above equation can be written as

\[
\frac{d^2 \psi(x)}{dx^2} = \frac{\rho(x)}{\varepsilon_0 \varepsilon_r} \tag{2.28}
\]

Applying Boltzmann distribution for the ions in the electric double layer, we have

\[
\frac{d^2 \psi(x)}{dx^2} = \frac{N_A e \sum Z_i c_i \exp \left(-\frac{Z_i e \psi}{\varepsilon_0 k T} \right)}{\varepsilon_0 \varepsilon_r} \tag{2.29}
\]

\(N_A\) is Avogadro's number; \(c_i\) is the bulk ionic concentration and \(Z_i\) is the corresponding ionic valence. For 1:1 electrolyte (\(c^+ = c^- = c\)). Accordingly, equation (2.29) becomes

\[
\frac{d^2 \psi(x)}{dx^2} = \frac{2N_A ze c}{\varepsilon_0 \varepsilon_r} \sinh \left(\frac{2e \psi}{k T}\right) \tag{2.30}
\]

For \(Z e \psi/k T \ll 1\),

\[
\frac{d^2 \psi(x)}{dx^2} = \frac{2N_A (Z e)^2 c}{\varepsilon_0 \varepsilon_r k T} \psi \tag{2.31}
\]

\[
\frac{2N_A (Z e)^2 c}{\varepsilon_0 \varepsilon_r k T} \text{ is equal to } \kappa^2, \text{ where } \kappa \text{ is known as Debye Huckel parameter. Thus,}
\]

\[
\frac{d^2 \psi(x)}{dx^2} = \kappa^2 \psi \tag{2.32}
\]

The solution of above equation is

\[
\psi(x) = \psi_0 \exp \left(-\kappa x\right) \tag{2.33}
\]

which is a simple exponential decay

The whole system should be electrically neutral, which is described by the electroneutrality condition.

\[
\sigma = \oint \rho \ dx = \varepsilon_0 \varepsilon_r \oint \frac{d^2 \psi(x)}{dx^2} = \left[ \varepsilon_0 \varepsilon_r \frac{d^2 \psi}{dx^2} \right]_{x=0} \tag{2.34}
\]

Equation (2.34) gives the relation between the surface charge density and potential on the surface. Taking value of \(\frac{d^2 \psi(x)}{dx^2}\) from equation (2.30) and then solving
equation (2.34), we get the relationship between surface charge density and surface potential in accordance with Gouy Chapman Theory.

\[ \sigma = (8RT \varepsilon_\varepsilon_0 c X 10^3)^{0.5} \sinh \frac{zF\varepsilon}{RT} \]  

Once \( \psi \) is known, the equilibrium constants for surface reactions can be calculated.

In present work DLM has been employed in the SCM of the sorption data. Since computing surface reaction equilibrium constants involves rigorous calculations, geochemical speciation code, FITEQL 4.0, has been used in present studies.

2.13.3. FITEQL 4.0

The best-fit equilibrium constants for surface equilibrium reactions were determined by modeling sorption data using the simulation code FITEQL 4.0. To solve sorption problems, laws of mass action and mass balance constraints are applied and chemical species concentrations are subjected to iteration until the difference between the calculated and observed values is minimized i.e. best fit solution of the derived set of nonlinear equations is achieved. This iterative numerical procedure, based on Newton Raphson approximation, typically computes a correct and unique solution; provided the geochemical equilibrium problem is mathematically defined in terms of adequate chemical components. The geochemical problem definition of components and species in FITEQL 4.0 is given in the form of Tableau (Dzombak and Morel, 1990; Morel and Morgan, 1971; Morel, 1983). In this format, every species can be represented as the product of reactions involving only components. Components are defined in such a manner that they cannot be obtained as reaction product of other components. The charge on the surface species is also defined as a component in tableau. For each convergent optimization, FITEQL 4.0 provides the
quality of fit criterion ($V_y$) for a set of surface constants. $V_y$ is the weighted sum of squares of residues (WSOS) divided by the degrees of freedom (DF), may be calculated using the equation:

$$V_y = \frac{\text{WSOS}}{\text{DF}} = \frac{\sum (Y_j/S_j)^2}{N_p N_c - N_u}$$  \hspace{1cm} (2.36)

where DF (Degree of Freedom) = $N$ (number of data points) – number of adjustable parameters, $Y_j$ is the mass residual balance calculated from the deviation between the calculated and experimental mass balance for the component $j$; $S_j$ is the error calculated for $Y_j$ from the experimental error estimates; $N_p$ is the number of data points; $N_c$ is the number of components for which both the total and the free concentrations are known; and $N_u$ is the number of adjustable parameters. The value of $V_y$ thus depends on the experimental error estimates and generally lies between 0.1–20 for satisfactory fit of the data, when realistic error estimates are used (Dzombak and Morel, 1990; Herbelin and Westell, 1994).

2.13.4. MINTEQA2:

In present work the speciation of metal ions in aqueous solution has been calculated using equilibrium speciation code MINTEQA2. A comprehensive database of components and species has been included in MINTEQA2. However, there is provision in MINTEQA2 to add new components and species. Moreover, it includes the implementation of a competitive Gaussian model for computing the complexation of metals by DOM. An ancillary program, PRODEFA2, serves as an interactive pre-processor to help produce the required MINTEQA2 input files. Like FITEQL 4.0, nonlinear optimization procedure is used to calculate speciation in MINTEQA2 (Allison et al., 1991).