Abstract

The present work focuses on investigation of photon-atom interaction processes in the X-ray energy region. The experimental measurements of X-ray fluorescence, Rayleigh scattering and radiative RRS processes in various elements were carried out using energy dispersive (ED) detection set up involving LEGe, Si(Li) and silicon drift (SDD) detectors, and photon sources based on $^{55}$Fe and $^{241}$Am radioisotopes source and Ag-anode X-ray tube. The high resolution wavelength dispersive (WD) detection set up consisting of an end window Rh-anode X-ray tube source, various diffraction crystals [LiF(220), LiF(200), PET, XS-55, XS-N and XS-C], and NaI(Tl) and gas flow detectors was used. Further, the X-ray diffraction (XRD) set up was also employed for chemical phase identification of elements present in samples related to various studies. Chemical effects on radiative $L_3M_{4,5}$ RRS cross sections and X-ray energies in $^{59}$Pr compounds were studied. The radiative resonant Raman scattering (RRS) cross sections for the $^{59}$Pr in $L_3$ subshell were measured and the alignment of the produced virtual $L_3$-subshell ($J = 3/2$) vacancy states was also studied through angular distribution measurements. The effect of chemical environment on the $K$ and $L_i$ ($i = 1$-$3$) subshell X-ray energies was also studied. The Rayleigh scattering cross sections for six photon energies ranging 36.8-52.1 keV were measured for the elements with $22 \leq Z \leq 90$. The measured Rayleigh scattering cross sections were compared with theoretical form factor formalism and S-matrix based calculations. As an application of radiative decay based X-ray fluorescence (XRF) technique, the elemental analysis was employed for study of Phytoremediation of $^{34}$Se contaminated soil using chick pea and wheat plants. Also, the response of plants to $^{33}$As added to same soil is studied. Elemental characterization of an antique ‘The Royal Silver Salver’ was performed using the EDXRF set up. Also, the traditional Ayurvedic Bhasma medicines were analyzed for elemental concentrations using WDXRF and for chemical phases using XRD for essential and potentially toxic metal contents.

Chapter 1 covers the theoretical approach of photon-atom interaction and subsequent inner shell vacancy decay processes. The foremost interaction processes, viz., photoionisation and scattering; and the inner-shell vacancy decay processes, viz., X-ray emission, auger electron emission and coster kronig transitions have been discussed. The near edge processes, viz., resonant Raman scattering (RRS) and extended X-ray absorption fine structure (EXAFS) are also explained. These processes become significant at the incident photon energies in the
vicinity of the ionization threshold of the target atom. The X-ray diffraction process is explained. The powder XRD gives information about the crystal lattice dimensions, which is further used to identify the chemical phase of the element present in the sample.

Chapter 2 includes the various experimental techniques and data analysis procedures used in the present work. Energy dispersive (ED) and wavelength dispersive (WD) detection based X-ray fluorescence techniques have been discussed. Different source-target-detector geometrical set ups involved in energy dispersive technique along with necessary detection set up used for present measurements are discussed in details. The working of pulse processing modules connecting the detectors to computer is discussed in detail. The methodology for data analysis, measurements of cross sections and elemental concentrations are also described herein. The X-ray spectra were analyzed for peak areas using an indigenously developed computer code involving the non-linear least square fitting routines for the multi Gaussian function with polynomial background. The incident photon intensity, detector efficiency and other geometrical factors were determined by measuring K-X-ray yields from targets of different elements and from the knowledge of respective fluorescence cross sections. Necessary corrections for the absorption of the incident and emitted X-rays in thin and thick targets are also discussed. Different target preparation methods used in the present work are included. X-ray diffractometer (XRD) set up employed for the detection of the various chemical phases of elements present in samples, along with its spectral analysis software has been discussed in detail.

Chapter 3 involves the study of chemical effects on radiative $L_3M_{4,5}$ RRS cross sections and X-ray energies in $^{59}$Pr compounds. The study involves measurement of radiative resonant Raman scattering (RRS) occurring in $L$ shell of the $^{59}$Pr element. The $L_3M_{4,5}$ radiative resonant Raman scattering (RRS) cross sections have been measured for the quasimonochromatic Mn $K\alpha_{1,2}$ X-rays (5.895 keV) in $^{59}$Pr ($L_3$-subshell level width ($\Gamma_{L3}$) = 3.60 eV) using targets in metallic and various chemical forms. The incident Mn $K\alpha_{1,2}$ X-ray energy is lower than the $L_3$-subshell binding energy of $^{59}$Pr by ~69 $\Gamma_{L3}$. The experimental measurements were performed with a low energy Ge detector (LEGe) and a radioactive $^{55}$Fe annular source in conjunction with $^{24}$Cr absorber. The measured radiative RRS cross section values for the $^{59}$Pr element in its various oxidation states are found to be same within experimental errors. The measurements were also performed to investigate alignment of the intermediate $L_3$-subshell ($J = 3/2$) virtual vacancy states in $^{59}$Pr through angular distribution measurements for RRS photon emission, which is found to be isotropic within experimental
errors. Further, the study of chemical effect on the $K$ and $L_i$ ($i=1-3$) subshell X-ray energies has been performed for $^{59}$Pr compounds. The measurements for shift in X-ray energies due to change in chemical environment were performed using 59.54 keV $\gamma$-ray photons from $^{241}$Am radioisotope source and an LEGe detector in case of $K$ X-rays from $^{59}$Pr. The measurements for shift in $L$ X-ray energies were performed using wavelength dispersive (WD) set up involving Rh-anode X-ray tube source and NaI(Tl) scintillator detector. The shifts are measured by relative shift of centroids for X-ray peaks for $^{59}$Pr compounds with respect to those of $^{59}$Pr element. The shift in $K$ X-ray energies is observed to be ~ few eV using energy dispersive (ED) system. In case of $L$ x-ray energies the shift values are expected to be small. From the present data, it is difficult to deduce regarding the trends in the shift values for the $L$ X-ray energies. More precise measurement techniques are required for the study of chemical effect in the $L$ X-ray energies. It is observed that the energy dispersive system with good resolution Ge/Si(Li) detector is more useful than WD system for the study involving chemical shift measurement for $K$ X-rays above 20 keV. In-vacuo WDXRF is certainly better for chemical shift measurements for low energy $K$ X-rays and $L$ X-rays.

**Chapter 4** includes the measurements of Rayleigh scattering differential cross sections for the 36.8 keV ($^{60}$Nd-$K\alpha_2$), 37.4 keV ($^{60}$Nd-$K\alpha_1$), 42.2 keV ($^{60}$Nd-$K\beta_{1,3}$), 45.2 keV ($^{66}$Dy-$K\alpha_2$), 46.0 keV ($^{66}$Dy-$K\alpha_1$) and 52.1 keV ($^{66}$Dy-$K\beta_{1,3}$) X-rays at an angle of 139°, in 44 elements with $22 \leq Z \leq 90$. The $^{60}$Nd and $^{66}$Dy annular foils along with $^{241}$Am radioactive source in secondary mode were used as photon sources. Intensity of the incident photons along with other geometrical factors were determined by measuring the isotropically emitted $K$ X-ray yields from standard targets of various elements with $22 \leq Z \leq 57$ in case of $^{60}$Nd secondary source and $56 \leq Z \leq 60$ in case of $^{66}$Dy secondary source. The relative efficiency of the detector was measured using $K$ X-ray yields from targets of elements with $56 \leq Z \leq 66$ in the energy range 32-52 keV using $^{241}$Am source on the place of $^{60}$Nd/$^{66}$Dy foil and further extended up to 105 keV using the $^{155}$Eu radioactive calibration source placed at the target position. The measured Rayleigh scattering cross sections have been compared with those based on various form factor formalisms and the state-of-the-art S-matrix calculations to differentiate between their relative efficacies. The scattering cross sections based on the modified form factor (MF) formalism exhibit large deviations for the elements with electron binding energies in vicinity of the incident photon energy, and these deviations smooth out on inclusion of the anomalous scattering factors (ASFs) to the MF values. The cross sections
based on MF formalism after including ASF’s are found to be on an average higher by ~ 8% as compared to the measured ones for all photon energies. The S-matrix values exhibit in general, good agreement with the measured cross sections for the elements with $22 \leq Z \leq 90$.

**Chapter 5** deals with the study involving Phytoremediation of selenium and arsenic contaminated soil using two types of plants, *viz.* chick pea and wheat. In the experiment the plants were grown in soil with known $^{34}\text{Se}$ and $^{33}\text{As}$ concentrations. Different combination of selenium and arsenic are added to the same soil. Fully grown chick pea plants and wheat plants grown up to seedling stage were used to check the uptake of $^{34}\text{Se}$ and $^{33}\text{As}$ in various parts of plants, *viz.* roots, stem and leaves. The uptake is studied by elemental analysis of various parts of plants using EDXRF set up involving mini X-ray tube with Ag anode as photon source and peltier cooled silicon drift detector (SDD) detector. To avoid the matrix effect in the plant samples the known standard for $^{34}\text{Se}$ was prepared using same matrix by spiking known concentrations of Se. Uptake of $^{34}\text{Se}$ is observed in both types of plants and there was no observable uptake for $^{33}\text{As}$. There is increase in $^{34}\text{Se}$ uptake with increasing the $^{34}\text{Se}$ concentration in soil. Further, selenium uptake increases in case of presence of arsenic additive in soil to counter the presence of arsenic. It is likely that selenium is supportive in defence mechanism of the plant against the toxic elements arsenic. Selenium is more organometallic and gets more accumulated in the vicinity of roots and become more bioavailable. With the growth of the plant, the roots intake selenium by adsorption processes. Roots further regulate it to stem where it is distributed to leaves. At the later stage of plant, selenium also becomes available to seeds. This uptake behaviour of plants can help in removing the elements like $^{34}\text{Se}$ from the soil through phytoremediation. The crop used for phytoremediation from a seleniferous place can be mixed with the crop from the places where soils have no selenium. This addition of crops in fix proportions can dilute the $^{34}\text{Se}$ concentration in diet. It can become bioavailable to human from the diet as essential phytonutrient. In addition, phytoremediation of arsenic is not possible using these plants.

**Chapter 6** involves the elemental characterization of an antique ‘The Royal Silver Salver’ is performed using EDXRF technique. Reflection mode geometrical set up involving 59.54 keV $\gamma$-rays from $^{241}\text{Am}$ radioisotope source to excite the target specimen and LEGe detector has been used. The salver had engraved artifacts on its front surface. From elemental analysis it was observed to made up of Ag-Cd alloy coated with Ag-Hg amalgam. The salver was claimed to be of Mughal Ira (16th-17th centuries). Thickness of the upper amalgam layer and the main plate has been calculated using the characteristic X-rays and
their absorption in the salver plate and in the upper layer of the amalgam.

Chapter 7 deals with the elemental analysis of traditional ayurvedic Bhasma medicines. The quantification of various elements present in six ayurvedic herbal medicines of bhasma family, namely, Abhrak bhasma, Godanti bhasma, Mandoor bhasma, Swarn makshik bhasma, Shankh bhasma, and Vang bhasma are procured from three well known brands, viz., Dabur India Ltd., Baidyanath Pvt. Ltd., and Divya Pharmacy have been analysed using WDXRF technique. The X-ray Diffractometer has also been employed for detection of various chemical phases of elements/compounds present in ayurvedic medicines. The major crystalline phases in ayurvedic medicine samples have been identified to be calcium (Ca), calcite (CaCO₃), anhydrite (CaSO₄) and oldhamite (CaS) for calcium, hematite (Fe₂O₃) and magnetite (Fe₃O₄) for iron, and cassiterite (SnO₂) and megawite (SnCaO₃) for tin. Abharak bhasm was identified to be containing a chemical phase for Pb, i.e. scoldamite (PbSO₃). Traces for lead were observed in Abhrak and Vang bhasma samples for various manufacturers. Large variations for concentrations of some elements in samples from different manufacturers have been noticed. It raises doubts regarding their ability to cure disease. Further investigations are required to understand bioavailability, toxicity and applicability of Ayurvedic medicines. Public assurance of the safety and quality of Ayurvedic medicines is a must.