Abstract

In the first chapter, basic aspects of ion atom collisions are discussed. Collisions of heavy ions with atoms define one of the most active areas of research within the vast field of atomic physics. In the last decades, the design and construction of accelerators needed for these experiments, as well as the theoretical description of ion-atom collisions has advanced considerably. Creations of vacancies in the inner most shells of the target atoms is one of the various processes associated with ion atom collision. The de-excitation of the vacant inner shells are characterised by emission of Auger electrons and/or characteristic x-rays. Many details of the atomic excitation accompanying the vacancy production by ion impact can be studied by examining the spectral distributions of the characteristic x-ray lines.

Particle Induced X-ray Emission (PIXE) technique is based upon the ionisation of target inner shell electrons due to their Coulomb interaction with the incident projectile ion and subsequent emission of x-rays characteristic to the target atom. Accordingly in a multielemental specimen, each element can be traced and identified by referring to its characteristic x-ray lines. This technique proves to be a precise analytical technique featuring high sensitivity and non-destructiveness. Protons of energy 2-4 MeV are found to be the most suitable ionising agent to use as the ionising agent in PIXE principle. Forensic science may be defined as the application of various scientific disciplines to aid the criminal justice system. The primary tools in the investigation of forensic cases have been observation and interpretation of physical evidence. Elemental analysis of the evidences is one of the most commonly used methods to differentiate and associate them with one another. The analytical technique used for such analysis must be highly sensitive, quite precise and accurate in addition to being fast and non destructive. Mass spectrometry and chromatographic techniques are the most commonly employed for elemental
analysis in forensic science. But PIXE technique has an edge above these by being non-destructive and multielemental in nature.

The second chapter contains a brief description on various theoretical methods those have been developed to describe the process of inner-shell ionisation in heavy ion-atom collisions by utilizing different approximation methods. The theories describe systematic expositions of the various mechanisms governing the inner shell vacancy production in ion atom collisions. The information about various microscopic and macroscopic aspects of ion-atom combinations is provided through ion-atom collision. Different models namely; Binary Encounter Approximation (BEA), Semi Classical Approximation (SCA), First Born Approximation (FBA), Perturbed stationary state approximation in both separated atom picture (ECPSSR) & united atom picture (ECUSAR) and the Geometrical Model (GM) has been discussed.

In the third chapter, general technical aspects involved in the experiments for inner shell ionisation measurements through ion-atom collision and elemental analysis using PIXE technique are discussed. The characteristic x-rays were detected using Si(Li) and HPGe detectors whereas, silicon surface barrier detectors were used to detect the scattered projectiles. Conventional nuclear electronics like preamplifier, amplifier, analogue to digital converter (ADC), current integrators etc. were used for signal processing and storage of experimental data. GUPIX software package developed at the University of Guelph, Canada was employed in the analysis of PIXE data. Particular experimental arrangements used at the Inter University Accelerator Centre (IUAC), New Delhi and Institute of Physics (IOP), Bhubaneswar to carry out the work presented in the thesis were discussed in detail.

In the fourth chapter, development of a new experimental setup for Ion Beam Analysis (IBA) at VEC, Chandigarh is discussed. The energy range of the charged particles available from the VEC, Chandigarh is ideal for ion beam analysis. The modifications and enhancements, carried out to develop a suitable facility to be used as a regional facility along with the standardisation and calibration of the new experimental setup for routine PIXE analysis are presented. Trace elemental characterisation of various specimens can be carried out using the new facility by PIXE technique. The specimen can be thin or thick; electrically conducting or
insulating and can be of any arbitrary shape and size. For thin specimens, the minimum detection limits (MDL) were found to be $< 0.5 \text{ ng/cm}^2$ which is satisfactory for most of the potential applications like art, industrial processing, forensics and biology. For electrically conducting thick specimens the MDL was amounted to be $< 2 \text{ ppm}$. This can be further enhanced for any selected range of elements by using suitable absorbers in front of the x-ray detector. Successful attempts were also made to monitor the backscattered protons from the target in order to detect the low $Z$ ($2 \leq Z \leq 13$) elements in conjunction with the PIXE measurement. Though qualitative assessment of the low $Z$ elements is possible from the backscattered spectrum, quantitative estimation becomes difficult due to unavailability of appropriate cross section data.

The fifth chapter summarises results of the $K$ and $L$ shell x-ray production cross sections measurements for rare earth elements induced by Li$^{3+}$ ions thereby observation of the effect of multiple ionization in radiative process. Furthermore, use of enriched isotopic targets to compare the intensity ratios of different $K$ x-ray lines to find out any signature of the effect of hyperfine splitting. The ion beam energy was kept above 3 MeV/u so that the effect of target sub-shell coupling resulting in rearrangement of the initial vacancies is avoided.

Apart from the intrinsic interest of ion-atom interactions, the investigation of the basic ion-solid collision is necessary to understand the various phenomena associated with it. Although both experimental and theoretical investigations of inner shell vacancy production have been carried for a long time, the process is far from being completely understood. Continuous improvements in different theoretical models are being carried out in order to incorporate different associated phenomena of ion-atom interaction. The predictions of these models are needed to be verified experimentally for better understanding of the inner shell vacancy production by heavy ions. This interest is due to the fact that inner shell ionisation cross sections are required in different kinds of applications such as calculation of stopping power, ion implantation, study of plasmas and PIXE technique for trace elemental characterisation of various specimens.

During ion-atom collision, ionisation of an inner shell electron of the target atom is produced by two processes; direct ionisation (DI) and electron capture (EC).
The DI process is essentially the direct transfer of momentum to the bound electrons of the target by the incident projectile ion due to the Coulomb interaction whereas EC process is due to the capture of a bound state electron of the target atom to an unoccupied state of the projectile ion. The DI process is independent of projectile charge state and is the principal mechanism of ionisation for \( Z_1 << Z_2 \) and \( v_1 >> v_2s \), where \( Z_1 \) and \( Z_2 \) refer to projectile and target atomic numbers while \( v_1 \) and \( v_2s \) (\( s = K, L, M... \)) are the velocities of the projectile and target inner shell electron respectively. The EC contribution to the target inner shell ionisation is dependent upon projectile charge state and becomes significant for \( Z_1 \leq Z_2 \) and \( v_1 \leq v_2s \).

The violent nature of the heavy ion collision creates multiple vacancies in the target atom. Aside from the increase in the electron binding energy that shifts the emitted x-rays towards higher energy, removal of the additional electrons in multiple ionisation affects the x-ray process by reducing the pool of outer shell electrons. The ionisation cross section also depends upon target thickness. As, for thick solid targets, vacancies in the projectile \( K \)-shell could be created, which enhance the EC process resulting in an increase of ionisation cross section. The \( L \)-shell ionisation as well as x-ray production cross sections using heavy ion beams indicates large deviations from theoretical estimates.

The \( K \) shell ionisation cross sections for Ti, Ni, Ba, \(^{157}\text{Gd}\), \(^{160}\text{Gd}\) and Au were measured with \( \text{Li}^{3+} \) ions of 28 – 45.5 MeV. The data were compared with the predictions of FBA and ECUSAR theories. In all the cases the ECUSAR theory provides a better agreement with the data in comparison to the FBA theory. In case of Au the ECUSAR predictions give a excellent match to the experimental data. For the Ti and Ni targets both the theories underestimate the data which can be attributed to the simultaneous multiple ionisation of outer \( L \) and \( M \) shells along with the \( K \) shells. Due to these vacancies in the \( L \) and \( M \) shells, the widths of both the radiative and non radiative transitions decrease. But the non radiative process being a two electron process, decreases more than the radiative process. Hence the effective fluorescence yield increases providing an enhancement in the x-ray production cross section. In case of data from Ba and two Gd isotopes, there was deviation from the theoretical predictions in the low energy regime, where the theoretical predictions
overestimate the data. At higher energies the ECUSAR predictions are closer to the data.

More extensive study with greater number of target elements are required to ascertain the phenomena proposed above. Also, the energy range of the incident ions has to be increased to observe the energy dependence of the multiple ionisation effect on K shell x-ray production.

The cross sections of L shell ionisation induced by 28-45.5 MeV Li$^{3+}$ ions were measured for Ba, $^{157}$Gd, $^{160}$Gd and Au. In this energy regime, the effect of intra shell coupling becomes negligible and the probability of multiple ionisation also considerably decreases. Different methods were incorporated to extract the ionisation cross section from the x-ray production cross sections. It was observed that, if there is enough statistics in the acquired spectra, the extracted ionisation cross sections will eventually be equal within the uncertainty of the respective atomic parameters irrespective of the extraction methods. In general, the data were closer to the predictions to the ECUSAR theory than the FBA theory. In case of Au, there are considerable differences between the data and theoretical predictions for the L1 subshell ionisation cross section. This discrepancy may be attributed to the effect of multiple ionisation of the Au M and N shells along with the L shell which is being responsible for the enhancement of the L shell fluorescence yields.

From the above observations it can be concluded that further measurements with greater number of energy points are required in order to get the energy dependence of the cross sections which in turn will enlighten if there is any other phenomena which may be playing a role for this discrepancy of data and theory. Additionally measurements with different incident ions are necessary in order to understand the projectile dependence of the process which can be used to verify the wave functions used in the theoretical calculations.

In the sixth chapter, details of the experiments and results of the elemental analysis of various specimens of forensic interest carried out using PIXE technique are discussed.

Physical and chemical investigations of gunshot residues (GSR) are being performed routinely in order to solve a number of forensic problems such as identification of gunshot wounds, estimation of time since discharge of a firearm,
distribution of GSR at the crime scene, estimation of shooting distance and establishing whether a person has fired a gun. Sensitive analytical methods are required for the identification of inorganic GSR that are usually present in very small quantities on a substrate. The PIXE analysis of gunshot residue profiles of the associated elements around the bullet hole for various firing distances showed to play a vital role in forensic science.

Elemental characterisation of GSR samples deposited of target was undertaken to find out any systematic behaviour in order to ascertain the type of firearm, ammunition or distance of firing in a forensic point of view. From the study of the samples taken by using small firearms, it was observed that the GSR deposited on the target is indeed different in terms of different elemental concentrations despite using same ammunitions. Therefore, can be proposed that, identification of firearm is possible from the analysis of GSR deposited on target provided, the uniqueness of the firearm is known. Extensive study is needed to be carried out and a database has to be prepared to ascertain the uniqueness of a firearm. In the present experiments the samples were from three different distances only. Therefore it was difficult to make a concrete observation in regard to the distance estimation although definite trend in the decrease of the elemental concentrations was obtained. Samples from greater number of firing distances has to be analysed to get a clear picture on this aspect.

In order to distinguish the compositional group, origin and authenticity of a gemstone; the combination of non-destructiveness, accuracy, sensitivity and high spatial resolution are required. PIXE is one of the few techniques that provide all these above features. Elemental analysis of geological samples, namely the gemstones, by PIXE technique, is challenging as the samples are insulating and inhomogeneous. Therefore, the effect of high bremsstrahlung background due to the charge build up on the sample and the elemental profile mapping at different regions of the sample due to its inhomogeneity are to be considered.

Garnet, citrine and peridots of both natural and synthetic origin were characterised using PIXE technique. The simple technique of using carbon tape to provide a grounding path and avoid any charge build up during the PIXE run is found to be satisfactory. Only from the elemental profile, it was possible to
differentiate the natural stones from their synthetic counterparts. The quantitative estimation of different elements provides an insight to the major, minor and trace constituents of different stones. This was found to be beneficial in order to establish the chemical constituent of the stone hence find out the actual mineralogical species. Also, from the quantitative analysis of the synthetics it is possible to obtain the matrix composition hence the actual material which was the basis for making the synthetic stone.

The counterfeiting of bank notes is a global problem that is increasing in scale and sophistication. Hence it has become very difficult to identify the fake by simply testing the look and feel of the paper. Also, it has been found that some contemporary counterfeits are printed using the sophisticated intaglio-printing method which is normally employed by the government agencies to produce their bank notes. It is therefore important to know the elemental and chemical composition of the paper and the printing inks that are used to manufacture and print bank notes. Understanding these two features of bank notes can assist in authenticating these items.

PIXE technique was employed to analyse different security features on the Indian bank notes of Rs. 500 denomination. Different elemental profile was obtained from the analysis of different locations. The elemental concentration showed good consistency for the notes of same series whereas there is considerable variation between different series. Due to legal constraints, it was not possible to analyse any counterfeit bank notes.

The above three applications of PIXE technique provided encouraging results that it can be applied in actual forensic investigations. Till date there is hardly any use of PIXE for forensic application. This technique being non-destructive in nature can also be used as a complimentary technique to enhance the quality of the data. With new PXIE facilities coming up it will not be difficult for the forensic scientists to use this technique as a routine procedure.

In the seventh chapter, the work presented in the thesis has been summarised.