TRACE ELEMENT ANALYSIS USING PROTON INDUCED EXCITATIONS

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Dedicated to my parents

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CHAPTER I

INTRODUCTION

The electric power generation in India has increased from 1362 MW in 1947 to about 105,000 MW as on March 2002, out of which about 62,000 MW is generated from coal-based thermal power stations. Over 100,000 MW additional generation capacity needs to be added by 2012 to bridge the gap between demand and supply of power. India, from early days depends on coal as a major source of energy for generating power, which is likely to continue as the main fuel for power generation. Use of coal brings own share of problems, primarily huge amount of ash is produced as a by-product of the process of electricity generation. The problem of ash management is quite complicated. A typical 200 MW unit produces ≈ 50-60 tonnes of ash per hour in India. Currently about 80 million tonnes of ash is produced annually. In future, a number of new coal based power plants are expected to be set up in order to match the ever-widening demand - supply gap of the power. It is expected that ash generation will reach a gigantic figure of 170 million tonnes per year by the year 2012 AD. This takes in to account the possible ash generation from the proposed projects and assumes an average ash content of 34% in coal [1].

Most of the coal based power plants were set up with the aim of power generation without considering the harmful effects of fly ash and the fly ash utilization. The part of the fly ash, which goes in air, leads to its consumption by human beings during breathing, and it is also being spread over a large agricultural area. However, a major portion of ash is disposed in wet form in ponds at coal fired thermal power stations. About 1500 million tonnes ash is estimated to have been dumped in ash ponds in India.

Almost all coal based thermal power plants in India adopt wet slurry ash transportation and disposal system. Bottom ash below the furnaces and fly ash collected from electrostatic precipitators are sluiced together with large amount of water and this ash water slurry is transported to ash ponds. In the ash pond, ash settles down and the effluent is led to natural water sources. This mixed ash is termed as pond ash. This method has been in vogue for many decades now all over the country.

At present, the fly ash is being used by cement manufacturers, brick manufacturers, farmers for mixing in fertilizers etc. Keeping in view the substantial use of this ash it is quite appropriate to have proper understanding of the trace element concentration, in fly ash. Trace elements, in general, may be defined as the elements of the periodic table which are found in very small quantities in a given sample. Generally in a given fly ash sample there may be a number of elements present. Some of them may be toxic ones and some may not. These toxic elements basically lead to harmful effects when consumed in sufficient amount over a long period of time. The trace elements found in fly ash give rise to potentially harmful effect on human health as well as it is toxic to other members of biotic community. As such, the study of trace element distribution in fly ash that is produced during coal combustion is important.

The Aligarh city is situated at about 130 Km from Delhi the capital of India and is an important industrial and educational center. It has a population of more than eight lacks and is well known for its lock Industry. Further, Aligarh is an important seat of learning. Aligarh Muslim University having more than 22,000 students and four postgraduate colleges affiliated to the Dr. Bhim Rao Ambedkar University Agra are situated in this City. Some eleven-kilometers from Aligarh there is a thermal power station at the village Kashimpur and another big thermal power plant is situated some 75 Km from Aligarh at Dadri in Ghaziabad district. Some 250 Km in the east of Aligarh there is another thermal power plant at Panki in Kanpur district. In the north about 40 Km from Aligarh there is Narora Atomic Power Plant (NAPP) in Bulandshahar district. In view of the large population in and around Aligarh and close by power plants it is desirable to have a data base regarding the pollution produced by the thermal power plants.

In view of the above, a program of measuring the trace element distribution in the fly ash produced from thermal power plants in the vicinity of Aligarh city has been under taken [2]. A brief introduction of different methods of trace element analysis is presented in Chapter II, while detailed review of the Proton Induced X-ray Emission (PIXE) method [3] is given in Chapter III. Experimental details including sample preparation, measurements and the analysis of the data is presented in Chapter IV of this dissertation. References are given at the end of each Chapter.

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CHAPTER II

Methods of Trace Element Analysis

2.1 Trace Element Analysis

The determination and characterization of trace elements in coal fly ash has received increasing attention in recent years because of its use in construction material, and for mixing with fertilizers etc. Not only that, fly ash is a major source of pollution near the thermal power plants because of toxic contents present in it. The electrical power generation industry in India is heavily dependent on coal based thermal power plants. The characterization of fly ash because of its potential for utilization and its potential as hazards to plants as well as animals have been reviewed by Adrino et. al. [1]. Fly ash, in general, is associated with various useful constituents such as Ca, Mn, Fe, Cu, Zn alongwith appreciable amount of toxic elements viz., Cr, Pb, Ni etc. It is recognized that health hazards and environment impact from thermal power plants result from the mobilization of toxic elements from the residues, which in turn mainly depends on meteorological parameters. As already mentioned, fly ash is used for cement making, in concrete mixing, and in making ceramic materials etc [2]. In view of the potential of fly ash as both a health hazard and a useful industrial raw material, studies of its elemental composition are highly desirable. The study of trace elements is being done in different fields; some of them are environmental studies including environmental pollution, biological sciences, forensic sciences, art and archeology etc. Trace elements may be present in any system in very small but unspecified quantities. As per the definition of trace elements, their concentration should be of the order of part per million (ppm) or part per billion (ppb). With the present day sophisticated instrumentation it is practically possible to detect elements with such low concentrations to a reasonable accuracy.

2.2 Methods of Trace Element Analysis

Material characterization without knowing its elemental composition is incomplete. Several chemical methods are available for separation of elements from the sample matrix before subjected to instrumental methods of elemental analysis. Several methods like solvent extraction, ion-exchange separation, reagent immobilized polymeric surfaces etc., have been widely used for trace element determination. In all these methods the element of interest is studied only after its separation. In such cases instrumental methods like Ultra Violet Spectrophotometer (UVS), Atomic Absorption Spectrophotometer (AAS), Atomic Emission Spectrophotometer (AES) etc., are useful. With the advancement in detection techniques, it is now possible to study the elements of interest from the sample without separating it from its matrix using highly sophisticated instrumentation. Some of the important techniques for elemental analysis are listed below.

2.2.1. Atomic Absorption Spectroscopy
2.2.2. Atomic Emission Spectroscopy
2.2.3. Neutron Activation Analysis
2.2.4. X-ray Fluorescence
2.2.5. Solid State Mass Spectroscopy
2.2.6. Proton Induced X-ray Emission

2.2.1 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS) is generally used to determine the presence of metals in liquid samples, typically in the concentration range of low mg/L. The technique uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame of graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. In their elemental form, metals will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular metal by focusing a beam of ultra violet light at a specific wavelength through a flame and into a detector. The sample of interest is aspirated into the flame. If that metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.

2.2.2 Atomic Emission Spectroscopy

Atomic emission spectroscopy (AES) uses quantitative measurement of the optical emission from excited atoms to determine analyte concentration. Atoms or molecules that are excited to higher energy levels can decay to lower levels by emitting electromagnetic radiations. The emission intensity of an emitting substance is linearly proportional to analyte concentration at low concentrations, and is useful for quantifying the emitting species.

Analyte atoms in solution are aspirated into the excitation region where they are dissolved, vaporized, and atomized by a flame, discharge, or plasma. These high-temperature atomization sources provide sufficient energy to promote the atoms into high energy levels. The atoms decay back to lower levels by emitting light. Since the transitions are between distinct atomic energy levels, the emission lines in the spectra are narrow. The spectra of multi-elemental samples can be very congested, and spectral separation of nearby atomic transition requires a high-resolution spectrometer. Since all atoms in a sample are excited simultaneously, they can be detected simultaneously. As such, concentrations of several elements present in the analyte can be determined in one experiment.

2.2.3 Neutron Activation Analysis

Neutron activation analysis (NAA) is a qualitative and quantitative multi-elemental analysis technique that depends on the capture of neutrons by stable nuclides converting some of them to radioactive nuclides, which decay by emitting characteristic γ-rays. The intensity of the γ-rays observed in the irradiated sample may be used to find the concentrations of the target nuclide. NAA can be done using the sample as received thus reducing or eliminating many potential errors and uncertainties associated with sample dissolution. Dissolution of the sample is generally not required in many applications. With its high neutron flux densities and nearly continuous operations, NAA compares to or exceeds the sensitivities attained by other elemental analysis methods, and can accommodate milligram to kilogram-sized samples, and in most cases, preserves the sample for additional analyses by NAA or other techniques. It is a non -destructive technique. In NAA procedure, the signal is induced when the nuclei of individual atoms capture neutrons to produce excited states that immediately decay by the emission of photons (prompt γ-rays). In most cases a radionuclide is produced that continues to decay according to its individual decay scheme and half-life through one or more excited states that also emit photons (delayed γ-rays). In principle either the prompt or delayed γ-rays can be used for both qualitative and quantitative analysis, however, in practice, use of prompt γ-rays in NAA is limited in application.

2.2.4 X-ray Fluorescence

When a primary X-ray excitation source from an X-ray tube or a radioactive source strikes a sample, the X-ray can either be absorbed by the atom or scattered through the material. The process in which an X-ray is absorbed by the atom by transferring all of its energy to an innermost electron is called the "photoelectric effect." During this process, if the primary X-ray had sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells and in the process give off a characteristic X-ray whose energy is equal to the difference between the binding energies of the corresponding shells. Since each element has a unique set of energy levels, each element produces X-rays of characteristic energies, allowing one to non-destructively measure the elemental composition of a sample. The process of emissions of characteristic X-rays is called X-ray fluorescence, (XRF).

2.2.5 Solid State Mass Spectroscopy

As far as semi-quantitative analysis is concerned, mass spectroscopy is a good technique. Here, the solid samples are used in the form of electrodes. A high voltage radio frequency spark discharge is established between two identical electrodes, due to which sputtering takes place and ions characteristic of the electrode material, are released from the electrode surface. They are then mass analyzed in a double focusing mass spectrometer. For multi elemental analysis, photographic detection is preferred. It may be noted that this method is a destructive method and the same sample can not be used for further studies [3].

2.2.6 Proton Induced X-ray Emission

Proton Induced X-ray Emission (PIXE) is an analytical technique capable of trace element detection sensitivity of a few ppm. When high-energy ions pass through matter, they interact with the electrons in the atoms and occasionally a vacancy is produced by the excitation of electron to higher energy level. When this occurs in an inner shell, an electron from an outer shell fills the vacancy, and an X-ray photon of characteristic energy is emitted. By measuring the X-ray energy, we can determine the atomic number, and the amount of the element present can be extracted from the area under the characteristic X-ray peak. For identification and quantification of trace elements, PIXE is several times more sensitive than most of the other techniques.

The main advantage of the PIXE method is the easy process of sample preparation, possibility of simultaneous multi-elemental analysis, short time of data collection, etc. In some cases the PIXE analysis may be treated as nondestructive. A brief review of the PIXE is given in Chapter III, of this dissertation.

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CHAPTER III

Review

3.1 Introduction

Atoms of different elements emit characteristic X-rays, when they are excited by creating the vacancies in their inner electron shells. Since each atom has its own structure of excited levels, the X-ray spectra of each atom is specific to the atoms. This characteristic X-ray spectrum may be used as a signature to identify the atom and the intensities of the characteristic X-rays may be co.-related to the concentration of the atom. The PIXE analysis is based on this method. In PIXE analysis, the electron vacancies are created by hitting the target atom with an energetic beam of protons. As a result of proton bombardment, characteristic as well as continuous X-rays are produced. The continuous X-rays as the name suggest, have a continuous energy spectrum, which depends on the energy of the incident proton beam. The characteristic X-ray spectra of different atoms present in the target are superimposed on this continuous background. Different theories have been employed to explain the process of X-rays production. Merzbacher and Lewis [1] explained the dependence of X-ray production cross-section on the energy and the atomic number using the Plane Wave Born Approximation (PWBA). Another theory proposed by Gracia [2], uses the binary encounter approximation according to which, the electron is considered unbound and the interaction of the energetic particles with this free electron is taken into account. Bang and Hansteen [3] gave a semi-classical treatment taking the impact parameter and particle deflection into account. The calculations done employing above theories agree fairly well with experimental data in a limited range of particle energy and target atomic number. An excited atom may also de-excite by other process as like Auger effect and Coster-Kroning transitions (transition between sub shells having same n values), in addition to radioactive transitions, leading to X-ray emission.

The X-ray production cross-section, σ_p for a line in X-ray spectrum is given by [4],

$$\sigma_p = \sigma_{ion}.\omega.k$$

Where,

σ_{ion} = Ionization cross-section

ω = Fluorescent yield and

k =The relative intensity of particular X-ray transition under investigation.

The foundation for use of the X-rays as elemental analysis tool was laid from the realization of the use of X-ray spectrometer. Later on many developments have been made by various researchers to use accelerated heavy charged particles instead of electrons or α-particles that exposed the possibility of elemental analysis by X-rays. During 1960,s Khan & co-worker [5], used protons for X-ray production and detection with the lithium-drifted silicon [Si (Li)], detector with a large solid angle. In 1970, Johansson showed that a combination of target excitation with ≈2 MeV protons and X-ray detection with a Si (Li) detector constitutes a very powerful method for multielemental analysis for trace elements. This new analytical method was soon popular by the name of Proton Induced X-ray Emission (PIXE), which has today made several developments in different analytical applications. PIXE is an analytical technique, capable of trace element detection with sensitivity of a few parts per million or even less with ability of detecting nearly all elements of the periodic table except the rare earths and low atomic number elements in a single run. In general, when ions pass through matter, they interact with the electrons in the atoms and occasionally, a vacancy is produced by an excited electron. When this occurs in an inner shell, the vacancy is filled by an electronic transition electronic transition from an outer shell, and an X-ray of characteristic energy is emitted. The energy of the emitted X-ray is characteristic for the elements in the sample and the amount of the element present can be known from the total counts in the peak.

3.2 Experimental set up

A PIXE set up consists of a electrostatic accelerator like Van de Graff or low energy Pelletron accelerator for proton acceleration, an analyzing and switching magnet, quadrupole magnet for focusing, a set of collimators, a target holder inside the scattering chamber and X-ray detecting and subsequent pulse analyzing system involving a Si(Li) detector, preamplifier, amplifier, multichannel analyzer and a PC based program for analysis of the data. A well analyzed and focussed beam of protons extracted from the accelerator is injected into the beam line through an analyzing magnet and then directed horizontally over a distance of several meters to the scattering chamber using electrostatic dipole or quadrupole magnets and steering elements. Finally, beam falls on the target after passing through a series of collimators in the scattering chamber. The pressure in the beam line and the scattering chamber is typically $\approx 10^{-6}$- 10^{-7} torr. For a beam of uniform intensity, either two pairs of deflecting electrodes which sweep the beam into perpendicular direction or a foil is used to diffuse it. The targets made up of sample to be analysed are usually mounted on a multiple target ladder oriented at 45° to the proton beam axis within the scattering chamber and are positioned in the path of the beam maintaining the required projectile - target and target - detector geometry of 45°. The preferred location for the Si (Li) detector is at 135° to the beam direction, because the intensity of bremsstrahlung background is significantly less than at the 90^{0}. The secondary electrons are emitted preferentially in the forward direction and bremsstrahlung emission is maximum at 90^0 to the beam direction. Beam charge measurements are generally carried out by charge integration from a Faraday cup. The Faraday cup is connected to the current integrator to measure the beam current that provides information about the number of particles that passed through the target during a certain time. Electron suppression is some times included, particularly for thick target work. In case of insulating targets, arrangement to prevent charging of the target is needed. The target can be sprayed with electron from the electron gun or sample is mixed with graphite powder while pallet preparation or coating of a thin layer of conducting material is usually done to avoid charging of target. Cold traps are included in some arrangements to condense any vapours in the chamber, which might contaminate the sample. With samples thick enough to stop the beam entirely, the specimen holder has to be insulated from the chamber and specimen connected directly to the charge integrator. In this case secondary electrons have to be returned to the specimen by a negatively biased suppresser electrode, typically at few hundred volt potential. Irradiations for about 5-10 minutes with a beam current of 5-50nA are good enough for a good statistics. The characteristic X-rays produced from the targets are collected using a Si (Li) detector with resolution of ≈150-180eV at 5.9keV X-ray of ^{54}Mn. The detector is placed as close as possible to the target. The characteristics X-ray spectra are recorded using a multi parameter analyzer. For the identification of X-rays, the multi parameter analyzer needs calibration prior to X-ray collection. A ^{241}Am X-ray source with wide range of X-ray energies is useful for calibration of the detector.

3.3 Basic Principle

PIXE is an analytical method based on X-ray emission. A Coulomb interaction takes place between the proton and inner shell electron resulting in the removal of K or L shell electron. The vacancy, thus created is filled by an electron from a higher orbit, an X-ray quantum is emitted, as schematically illustrated in Fig.3.1, subject to quantum mechanical selection rule viz.,

$$\Delta l = 1, \Delta j = 0, 1 \text{ and } \Delta n \neq 0$$

Where,

n is principal quantum number,
l is the orbital angular momentum and
j is the total angular momentum.

The shells are designated as K, L, M, N, O for n=1, 2, 3, 4, 5. The total angular momentum J is the vector sum of orbital angular momentum l and the spin s of the electron. i.e., $J = l + s$

The electron energy depends on both n and j. For the different values of n, l takes different values. For example, n=1,2,3...n etc, l= 0,1,2,3....(n-1). Consequently, J has different values depending on n and l. Thus, each shell except the K shell (n=0 and l=0), has sub shell for different J values; e.g., L shell has three sub shells; L_I, L_{II}, L_{III} because here n=2 which implies l=0, 1. Therefore, $j = l + s = ½,½,¾$.

Figure 3.2, shows a typical level diagram of X-ray transitions that are permitted by the quantum mechanical selection rules. The transitions coming to K shell are known as K X-rays and that to L shell as L X-rays. The X-rays originating from the electronic transition from the L- shell to the K-shell are usually

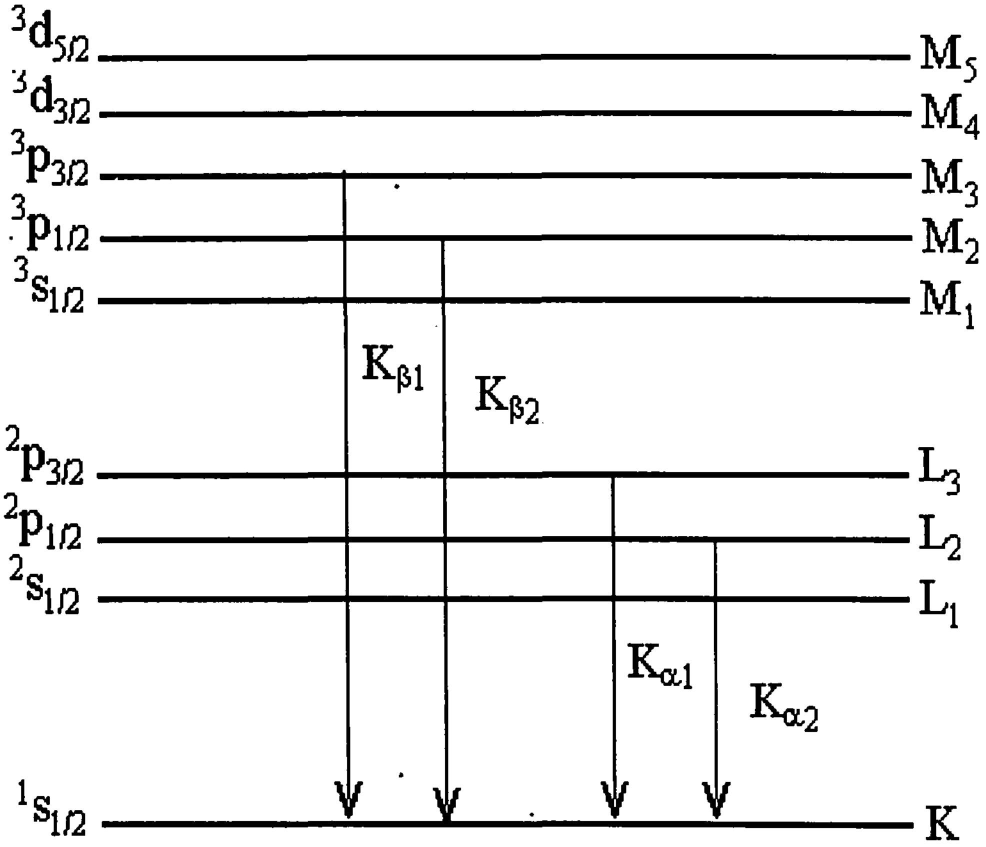


Fig. 3.2 A typical energy level diagram

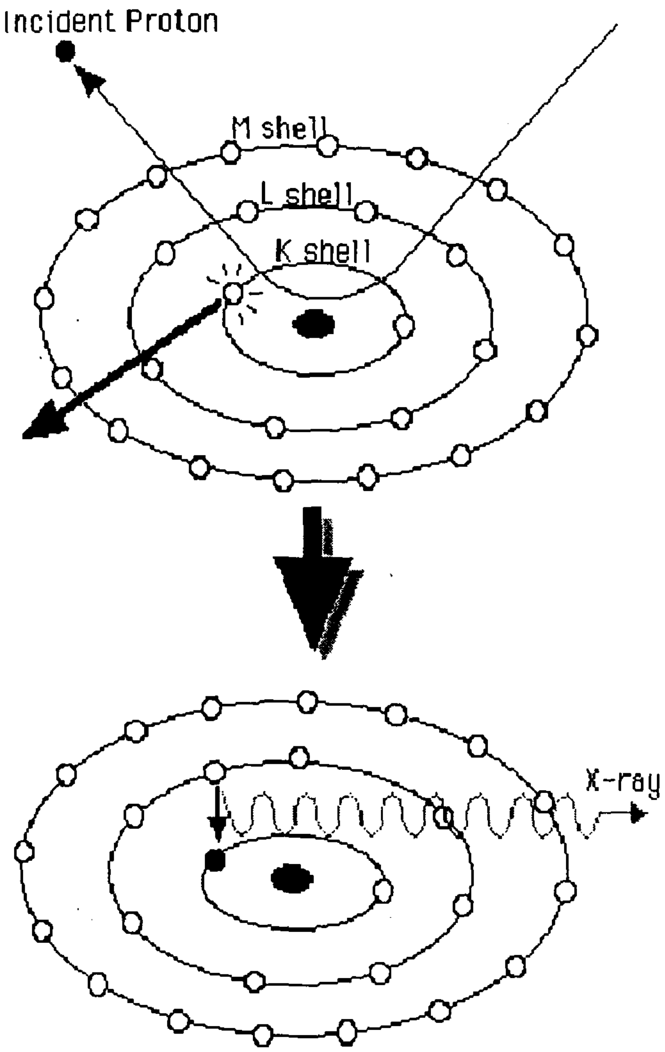


Fig. 3.1. Schematic of inner shell vacancy creation and subsequent X-ray emission due to proton bombardment.

referred to as K_{a1} and the transition from the M-shell is called K_{a2} according to the Siegbahn notation. Similarly for L X-ray, if electron comes from M shell, it is denoted as L_{a1} and if from N shell than L_{b2}.

3.4 Sensitivity

Sensitivity, in general, may be defined as the minimum detectable concentration from where the minimum detectable absolute amounts of several elements can be calculated knowing the weight of that part of the sample, which is irradiated by the proton beam. Of course, the results of such calculation depend on the experimental conditions. Some of the parameters which influence the sensitivity are the solid angle 'ω', detector resolution 'ΔE', collected charge 'J', and target thickness 't' etc, the variation of sensitivity on these parameters is given as,

$$\sim \Delta E^{1/2} (\omega j t)^{-1/2}$$

In order to show the kind of sensitivity one can obtain with the parameters,

$$\Delta E = 1.65, \qquad \omega = 0.003\times 4\pi, \quad J = 10\mu c, t = 0\ .01 mg/cm^2$$

the minimum detectable concentration values are shown in Fig. 3.3 (a). There are a number of parameters such as bombarding energy, beam current, measuring time etc., which have to be chosen rather carefully if optimum conditions are to be obtained. In this figure theoretical curves for the sensitivity as a function of the atomic number for two different bombarding energies are shown. In principle, in order to obtain maximum sensitivity, the energy of incident beam must be adjusted according to the element to be determined.

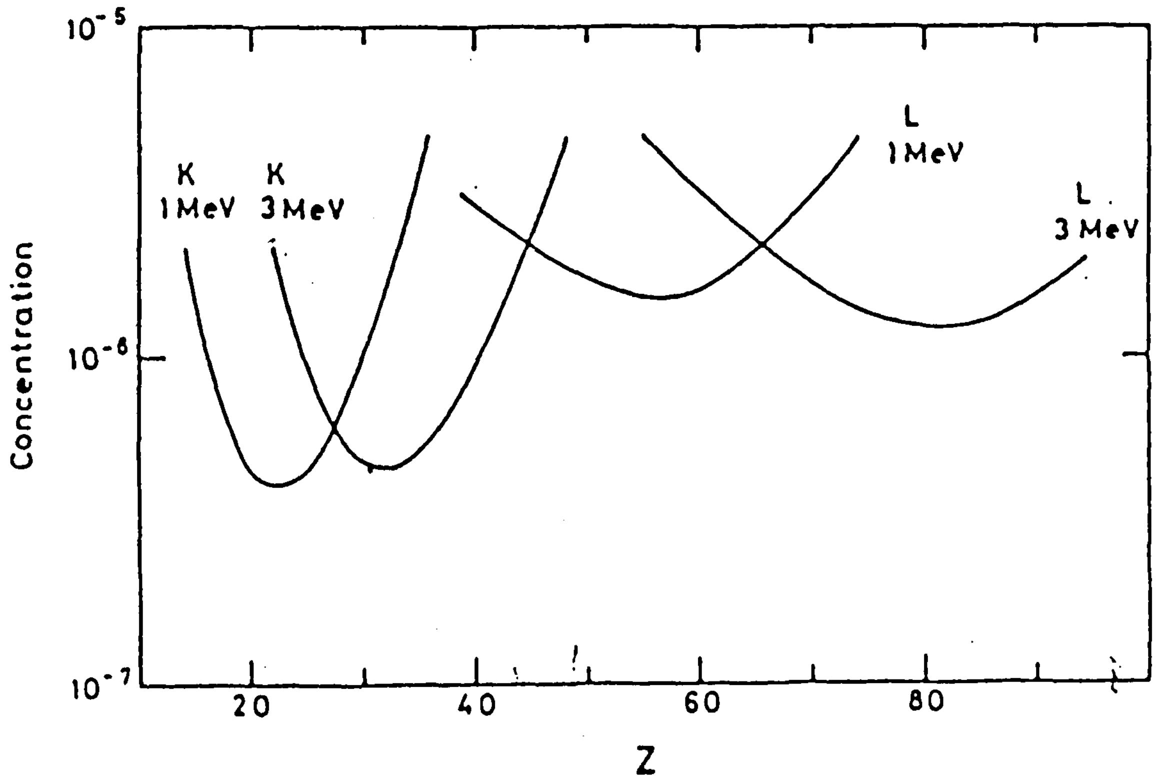
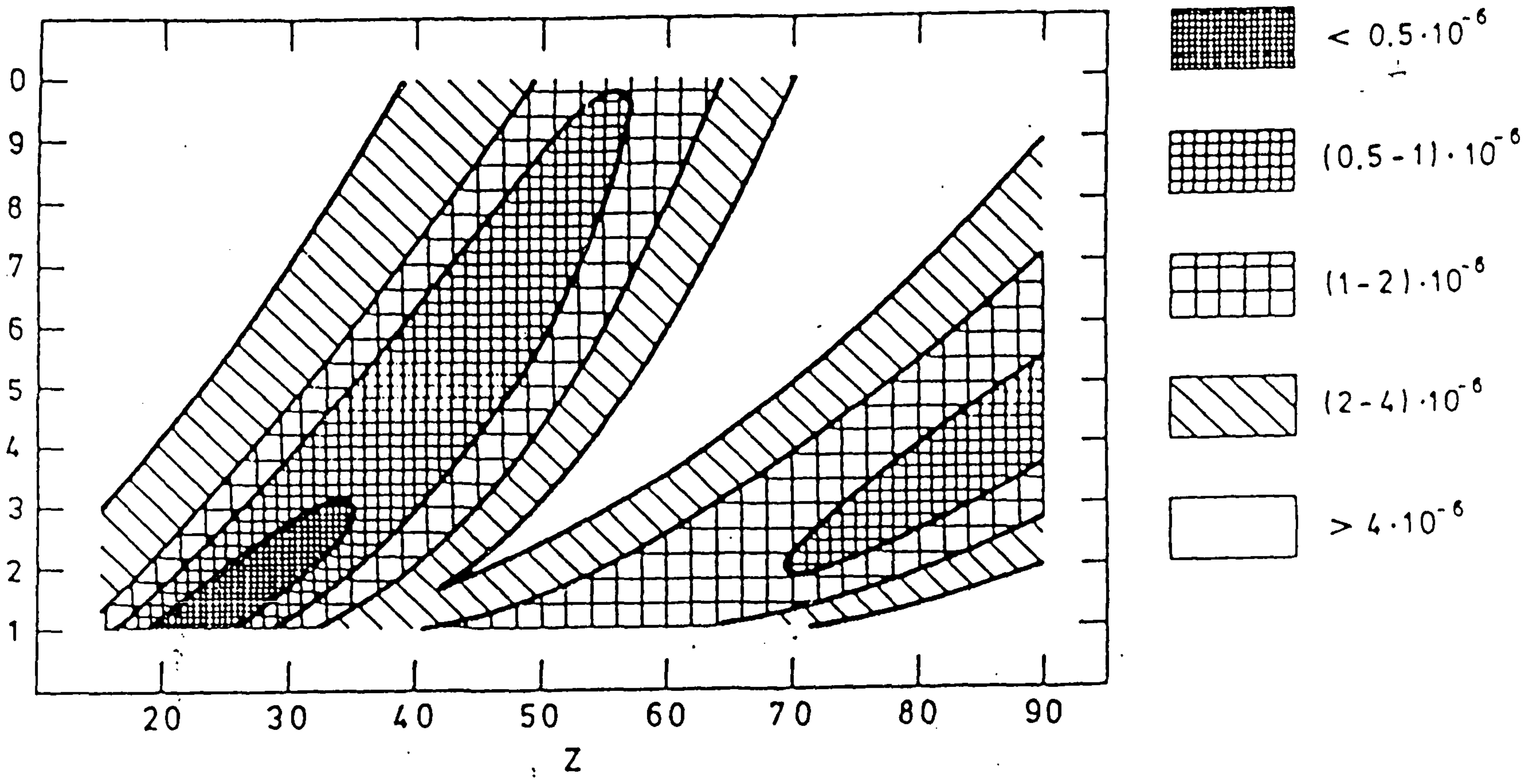


Fig.3.3 (a) Minimum detectable concentration as a function of atomic number for proton energies 1 and 3MeV.

Hence, in practice, the bombarding energy is so chosen that gives the best overall sensitivity. A clear picture of how the sensitivity varies, as a function of the bombarding energy and atomic number, is shown in the figure 3.3 (b).

It is clear from the Fig. 3.3 (b) that for the reason mentioned above the optimum energy is about ≈2 MeV. It will be noted that for this energy the sensitivity does not deviate very much from the mean in either direction. Such constancy in the sensitivity over practically the entire periodic table is, of course, a great advantage in analytical work. The resolution of the detector 'ΔE' is more or less fixed and the solid angle 'ω', subtended by the detector ought to be as large as possible. So, the only limitations are the geometry's of the irradiation chamber and the detector. The collected charge 'J' must also be maximized for optimum sensitivity. This can be done in two ways i.e., either by increasing the time of measurement or beam current. A rather normal choice is ≈ 10-20 minutes of irradiation, since with increased beam current the chances of excessive heating and deterioration of the target is not avoidable.

As can be seen from Fig 3.3 (b) the lighter elements have less sensitivity mainly due to the fall-of the fluorescence yield. The decreasing sensitivity for the heavier elements depend on the fact that for these elements X-ray cross-sections are decreasing while the background is relatively constant. Furthermore, it is clear that the position of maximum sensitivity depends on the energy of the incident particle. Within certain limits one can, therefore, adjust the proton beam energy to maximum sensitivity for a particular trace element. Another interesting fact of practical importance is that the higher sensitivity is obtained for Z ≈ 20-30, which happens to be the region of greatest interest in many applications. The limits of detection may be expressed absolutely, i.e., in terms of mass or concentration, which is usually expressed in ppm. In absolute



(b) Minimum detectable concentration as a function of atomic number and bombarding energies.

terms PIXE is an extremely sensitive method in the two atomic number regions ($20<Z<35$ and $75<Z<85$), which happens to contain the majority of trace elements of interest.

A very important factor, which limits the sensitivity of the analysis using PIXE, is background radiation. Even the analysis done using a 100% efficient detector and a very pure sample, this background affects the results. In case of the thick samples the background is attributed due to the organic or inorganic matrix in which the trace elements are embedded. If it is possible to remove the back ground completely, then elements of ultra low concentrations could have also been detected accurately. The continuous background at the base of the characteristics X-ray peak determines the limit of detection of an element. The background arises mainly due to proton bremsstrahlung, electron bremsstrahlung and nuclear reaction γ-rays. The bremsstrahlung produced in PIXE is mainly due to secondary effect i.e., electron bremsstrahlung and not the primary background contribution as in electron microprobes and X-ray fluorescence analysis. Perhaps the main reason for high sensitivity of trace element detection in PIXE is the reduced bremsstrahlung background compared to the electron microprobe. The intensity of primary bremsstrahlung emitted by a charged particle is proportional to the square of its deceleration. The Coulombic forces are the same for electron and proton but the masses differ by a factor of 1836; as a result the bremsstrahlung intensity due to proton is negligibly small in comparison with that of the electron in electron microprobe analysis. The increased signal-to-noise ratio allows trace impurity detection down to 1 ppm or less up to two orders of magnitude better than electron microprobes.

For most matrices the charge to mass ratio is close to ½. This means that this background contribution vanishes for α-particle and heavier ions but not for protons. When the incident particles have sufficiently higher energy to excite the nuclei in the target, γ-radiation will be emitted, giving rise to a high energy tail in the spectrum due to Compton scattering in the detector. The importance of γ-background can be seen in the work of *Folk Mann et al.*[6], it is dominant for Z>30 at proton energies 3 and 5 MeV. Therefore, the bombarding energy must be so chosen to give minimum γ-ray background, while still giving a reasonably large characteristics X-ray yield. A third important source of the background is the Compton scattering of gamma rays resulting from the excitation of nuclei in the target. Due to this a high-energy tail is absorbed in the spectrum. The composition for the target is important as far as gamma radiation is concerned, since some nuclides like F^{19} Na^{23} etc., have a higher gamma cross-section in the proton energy range that is usually employed.

Another source of the background is the radiation emitted in filling a vacancy in the molecular orbital, which exists during the collision. The energy of this orbital depends on the inter nuclear distance and the radiation emitted will, therefore, be continuous. Heavy ions can ofcourse also produce γ-radiation, which give continuous Compton distribution in the detector.

The X-ray energy spectrum consists of a continuous background with characteristics X-ray lines of the atom present in the sample. It has been found experimentally that a continuous background exists at low radiation energies but decreases once this energy becomes larger than the maximum energy that can be transferred from the projectile to the electron. This maximum kinetic energy is given by,

$$T_{\max} = \frac{4mE_1}{M_1}$$

Where, M_1 and E_1 are the mass and energy of the projectile respectively and m is the mass of the electron.

The bremsstrahlung from the projectile (protons in this case) is produced because of larger acceleration due to collision between the proton and the nuclei of the matrix atom. The cross-section for this is given by,

$$\frac{d\sigma}{dE_r} = C\frac{AZ^2Z_1^2}{EE_x}\left(\frac{Z}{A} - \frac{Z_1}{A_1}\right)$$

Where, A, Z and E are the mass, charge and the energy of the projectile and Z_1 and A_1 are the charge and mass of the matrix atoms respectively. E_r is the energy of the bremsstrahlung proton and C is a constant that is given by,

$$C = 4.3 \times 10^{-4} \log\left[\frac{4E_1}{Z_1 ZE_r}\left(\frac{E_1}{A_1} \times 100\,keV\right)\right]$$

where, b is an energy dependent variable given by,

$$b = \frac{4E_1}{A_1 - 2mVV_1}$$

where, A_1, E_1 and V_1 are the mass, energy and the velocity of the projectile and m and V are the mass and velocity of the electron respectively.

3.5 Calibration

In order to obtain quantitative results the peak areas in the X-ray spectra have to be normalized with respect to the integrated charge on the sample during the irradiation. The normalized peak area multiplied with a calibration factor gives the actual concentration. The integrated charge is measured using a charge integrator connected to the sample ladder as mentioned earlier.

3.6 The use of standard

Because of the lack of precise knowledge of critical system parameters such as absolute detector efficiency, X-ray filter attenuation and integrated beam current, many PIXE systems rely on standards to determine accurate specimen compositions. Although good results are obtained by various researchers running in standardless mode for a variety of samples of known composition. However, it is advisable to have a standard or set of standards in close approximation to that of the specimen. Many times it is easy to develop an internal standard to fit a particular measurement. The calibration factors are experimentally determined for each element by utilizing international standard reference materials of the same type as the sample.

3.7 Accuracy of measurement

Tests of the accuracy that can be obtained by PIXE method have been made by Campbell et.al.[7]. They analyzed Fe, Cu, Zn, and Pb in animal liver by PIXE and atomic absorption spectroscopy and found overall good agreement 10%. Bearse et.al., [8], analyzed Zn in whole blood with same methods and arrived at ≈10% accuracy. For Fe or Pb in samples of non-uniform kidney medulla tissue, Campbell et al. [9], found very poor agreement between Atomic Absorption Spectroscopy and PIXE. But the same work reported PIXE analysis of NBS orchard leaves standard and showed good agreement on the average although the individual fluctuations were large.

3.8 Interference

The large number of X-ray lines and the limited resolution power of Si(Li) detectors makes line interference unavoidable. Fortunately, in most analytical situations there are methods to handle these problems. A frequently encountered interference problem is that between K_α of the element Z and K_β of element (Z-1). This interference occurs in the transition region where the detector resolution separates K_α from K_β for element Z. For higher Z elements the energy difference permits the detectors to separates these interference lines. From Z values around 35 and up, the interference between L-lines from these elements and K- lines from lighter elements have to be considered. As the relative K-line intensity from one element is constant no matter whether excited by photons, electrons, protons or alphas, we may use uninterfered lines for successive unraveling of the spectrum. This works well for Kα-Kβ resolutions but calibration experiments are needed for determining the magnitude of L-and M-lines when their respective K-or L-lines are detected.

For aerosol analysis, Ba-Ti and Pb-S interference are the most difficult to handle.

3.9 Quantitative Analysis

Manually estimating the total number of counts under a peak subtracting the background counts gives the actual concentration. However, this is a tedious process with spectra containing many peaks. A computer code, which fits a Gaussian with exponential tail to each peak and a polynomial to the background serve the purpose best. GUPIX is a popular PIXE spectral data analyzing software, that models a theoretical spectrum of a particular element using the data base of K, L and M X-ray energies, relative X-ray intensities, fluorescence and Koster-Cronig probabilities which is then fitted with the experimental spectrum with respect to the known matrix. The software package provides non-linear least-square fittings of the spectrum, together with subsequent conversion of X-ray peak intensities to elemental concentration via a defined standardization technique involving X-ray energy dependent H values, relative charge and user-defined instrument constants. The software takes care of matrix effect, proton stopping power, X-ray mass attenuation coefficient and secondary fluorescence contribution for spectral fitting. The concentration of an element (C_z) is given as[9],

$$C_z = Y_m / [Y_t \{HQ\mathring{a}T\}]$$

Where, Y_m and Y_t are the measured and theoretical X-ray yields respectively, Q is the real charge accumulated, $\mathring{a}$ is the intrinsic efficiency of the detector and T is the transmission through absorber between target and detector. H value is the product of detector solid angle and a charge correction factor. Dutta *et. al.*

[10], have shown that H values are lower for low energy X-rays and become almost constant for Z=28 onwards.

3.10 External beam PIXE

The normal methods of placing the samples in evacuated irradiated chamber has some disadvantages. The main problem being that of the target preparation. Liquid samples have to be evaporated to dryness and samples containing water, e.g., organic tissue, deteriorates in vacuum. A solution of these problems might have to use an external beam. Several attempts to explore this technique have been made. The great advantage of an external beam is the simplified sample preparation and handling. Any type of sample can be irradiated directly and sample changing is easy. Sample may be more effectively cooled at atmospheric pressure than in vacuum. Deconninck [11] used an arrangement in which the proton beam was taken out from the vacuum beam line through a nickel foil and allowed to enter in an irradiation chamber filled with helium at the atmospheric pressure. Gronvall [12] used an external beam for the analysis of the water solution.

3.11 Applications

In general, PIXE can be characterized as a quantitative, accurate, and highly sensitive method for non-destructive method of multi elemental analysis of materials. Today, PIXE is well known for trace elemental analysis of samples of various types such as, biological tissues, plant materials, aerosols, fly ash, minerals, rocks, sand, water samples, paintings, plastic, polymer, ink, semiconductor materials etc.

Accuracy in PIXE analysis demands the best possible counting statistics, and so the limited counting rate capability of Si (Li) detector should not be wasted on spectral region carrying information of no interest. X-rays from elements below sodium cannot be seen because they are absorbed in either the detector window, the atmosphere between the sample and the detector, or through any filters used. A Mylar absorber of thickness ≈100-200 microns is frequently used to attenuate the intense bremsstrahlung contribution at X-ray energies below 4 MeV. For trace element analysis, often a filter is chosen to attenuate the X-rays at the energies of the major elements allowing the detector to measure the trace elements with greater sensitivity. Usually these filters will cause insensitivity to lighter elements, but will allow simultaneous analysis of any element above the filters absorption edge.

X-ray peaks from major elements can occupy much of the detectors useful counting capability. Dominant low energy X-rays may be filtered out so that the detector will only see contributions due to the higher energy trace or minor elements. Beam current may now be increased with an overall effect of much greater trace element sensitivity while keeping the detector at a low count rate. In some cases single element foils may be used as "notch" filters to attenuate only a dominant matrix element but allow relatively high transmission of all other X-rays. A good rule of thumb in this case is that the best absorbing filter is lighter than the dominant matrix element by 2 atomic numbers. That is to say that the best filter for a Fe matrix would be a Cr foil. With geological specimens where the K X-rays of Na, Mg, Al and Si dominate the spectrum and aluminum absorber ≈100 microns thick removes these, while transmitting most of the X-rays from interesting trace element of higher atomic number.

At very high-count rates, Si (Li) X-ray detectors will behave in a less than ideal fashion. Energy resolution could become significantly worse causing peaks to overlap. At the sufficiently high counting rates, pair of X-ray events that fall within the resolving time of the electronic system are summed to produced an apparent single event, resulting in a continuum to the right of the characteristic peaks of a given element. This pile-up can cause significant spectral distortion at counting rates as low as 1000 counts per second. Pileup peaks may appear which manifest themselves as multiples of principle peaks.

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CHAPTER IV

Measurement and Analysis

As part of a program of measuring the trace element concentrations in fly ash produced from different thermal power plants, the trace elements concentration measurements in the fly ash from the following three thermal power plants has been done using proton induced X-ray emission.

1. Harduaganj Thermal Power Station, Aligarh.
2. National Thermal Power Corporation (NTPC), Dadri, Ghaziabad.
3. Panki Thermal Power Station, Kanpur.

4.1 Sample Collection

Several fly ash samples have been collected from three Thermal Power Stations near Aligarh. A list of samples is given in Table 4.1.

The fly ash samples collected from Harduaganj Thermal Power Station (HTPS) are represented as AC and AO. AC represents samples from current deposits and AO represents deposits of ~10 years. For the present study 2 fly ash samples were collected from the fresh deposit site AC inside the plant near furnace, namely AC 1 and AC 2 in the month of May 2002. Three samples viz., AO1, AO2 & AO3 were collected from old deposit site AO out side the plant, near Jawan block about 4Km from the HTPS, Aligarh. NTPC represents fly ash samples from current deposits of National Thermal Power Corporation, Dadri, Ghaziabad and PN represents deposits from Panki Thermal Power Station, Kanpur. From NTPC Dadri, Ghazibad site, 4 samples viz., NTPC1, NTPC2, NTPC3 and NTPC4 were collected. Two samples PN1 and PN2 were collected from the site of Panki thermal power station, Kanpur.

Table 4.1: A list of samples collected from different sites

S. No.	Name of Thermal Power Stations	Samples
1.	HTPS, Haruaganj	AC 1 AC2 AO1 AO2 AO3
2.	NTPC, Dadri	NTPC 1 NTPC 2 NTPC 3 NTPC 4
3.	Panki, Kanpur	PN 1 PN 2

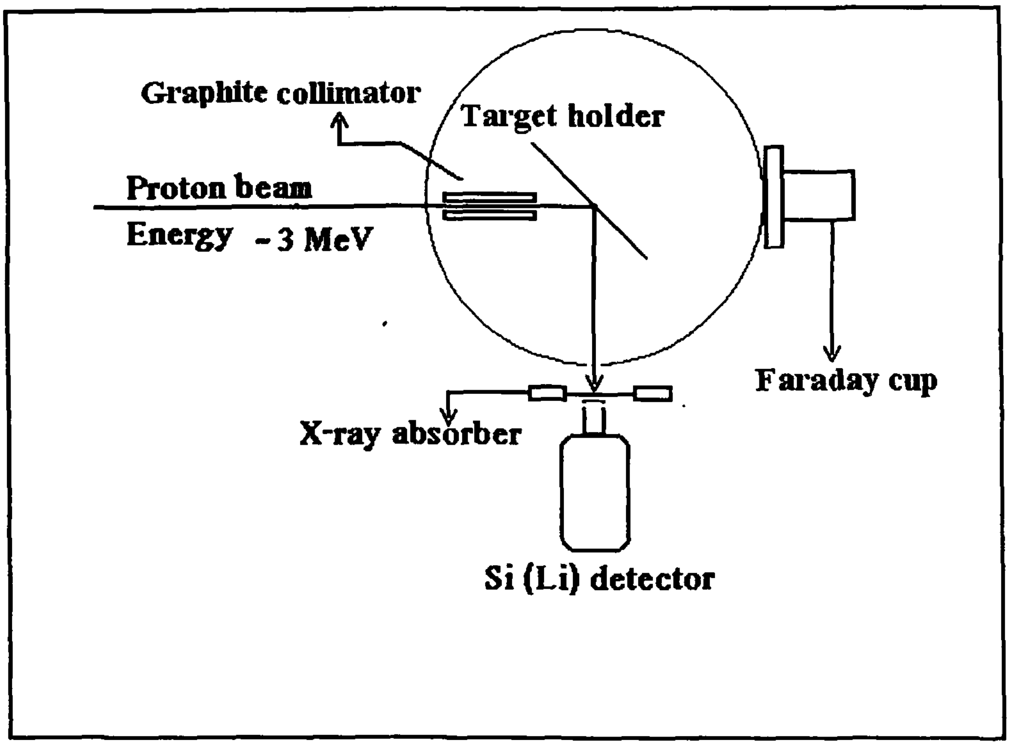


Fig. 4.1 A typical experimental set up for irradiation of samples.

4.2 Target preparation

Target preparation is one of the important aspects in PIXE analysis. The fly ash was filtered using a fine sieve. It was then dried at 35^0C to remove moisture from the ash. For preparation of the targets the samples were grinded and homogeneously mixed with standard graphite material in the ratio 1:1. Finally, a pellet of diameter 10 mm and thickness 1mm was prepared using hydraulic pressure machine by applying a pressure of $\approx$110kg/m^2. Similarly, a pellet was made from standard graphite powder obtained from Merck, Germany. One more similar pellet was prepared from the standard fly ash material obtained from National Institute for Standard and Technology (NIST), USA, and was used as a standard for the analysis of fly ash samples.

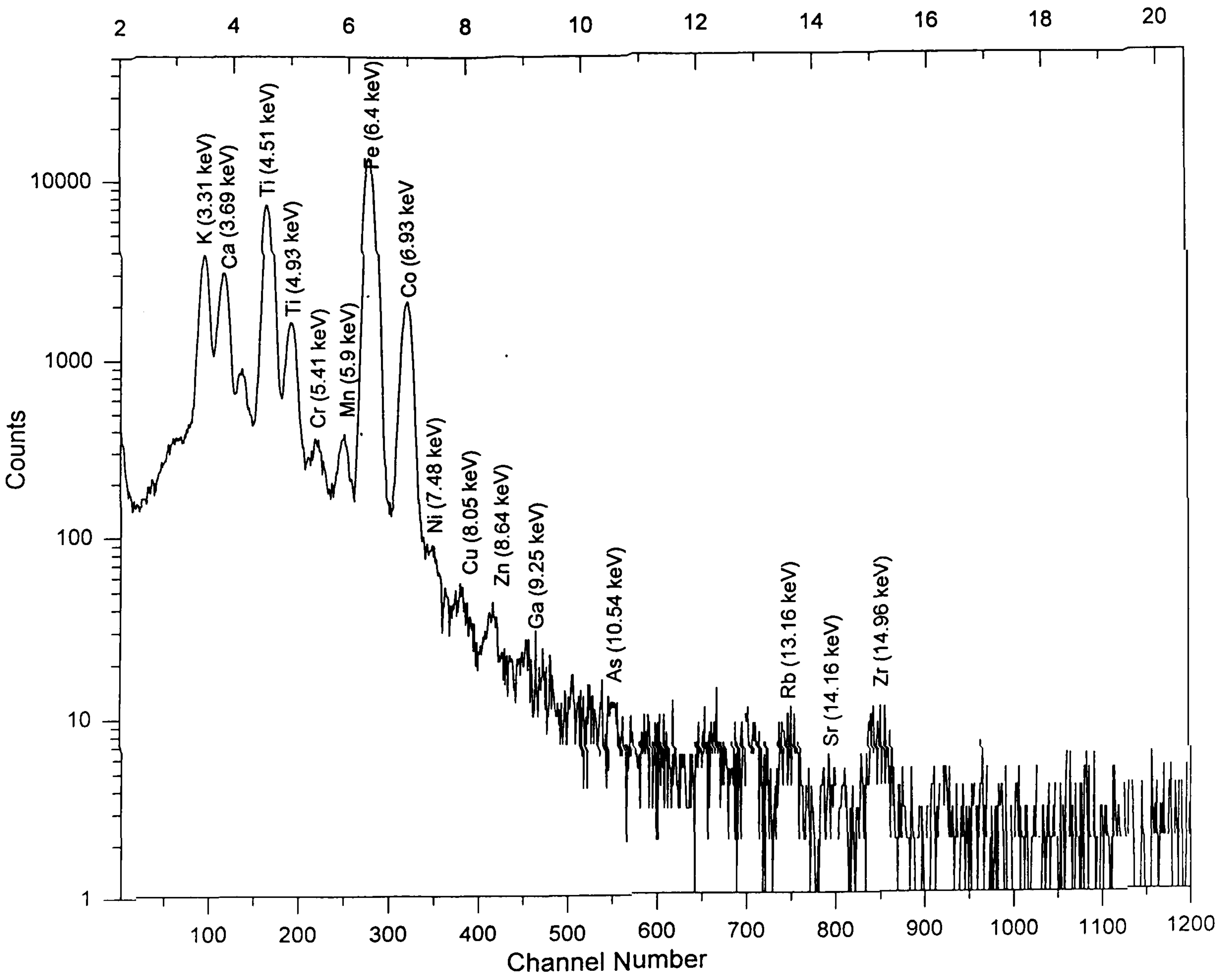
4.3 Experimental set up

A collimated proton beam of energy 3MeV taken from the 3UD Pelletron Accelerator at the Institute of Physics, Bhubaneswar, India was used for irradiation. The terminal potential was 1.495MeV. The targets were mounted on multiple target holder ladder oriented at 45° to the beam direction. The targets were positioned one by one in the path of the beam by moving the ladder vertically up and down maintaining the required projectile - target - detector geometry inside the scattering chamber maintained at a pressure of 10^{-6} torr. A typical experimental set up is shown in Fig 4 .1.

Each sample was irradiated for $\approx$20-30 minutes with different beam currents (3.5-25nA) maintaining the count rate at approximately 1000 cps in each run. X-rays produced from the beam-target interaction were detected using Si (Li) detector (EG & ORTEC), having active surface area of 30 mm^2, beryllium window of thickness 8μm and resolution of 180 eV at 5.9 keV of Mn X-ray. A 50 μm mylar window .was used to isolate the pressure of the scattering chamber from the atmosphere. The detector was placed at a distance of 8.5 cm away from the target in the air at an angle of 90° with respect to the beam direction.

The characteristic X-ray spectra were recorded using a PC based Canberra 88 series multi parameter analyzer in 2K-channel mode. The detector was calibrated using ^{56}Fe standard X-ray source prior to recording X-ray spectrum of the samples. Typical X-ray spectra recorded for all the samples of HTPS (Aligarh) and NTPC, Dadri, Ghaziabad without absorber are shown in Figs 4.3.1- 4.3.8. Since the intensities of the low energy X-rays were significant, it was expected that some X-rays from high atomic number elements, which may be presents in trace amounts may be hidden in the background due to the low energy X-rays in these spectra.

In order to decrease the low energy background and X-rays from matrix elements (e.g., K, Ca), spectral data were also collected from every sample through a 50μm aluminum absorber placed in front of the detector. Spectra recorded for all the fly ash samples collected from the various thermal power plants with the aluminum absorber are shown in Figs. 4.3.9 - 4.3.19. As can be seen from these figures that the low energy X-ray peaks are absorbed while the high-energy peaks have become much clear. It may be pointed out that the spectra of fly ash samples from panki thermal power station, kanpur could be recorded only with absorber. These samples could not be irradiated further to get spectra without absorber, as there was a major accelerator breakdown. These samples will be analysed in the next beam time run. As


2
4
6
8
10
12
14
16
18
20
K (3.31 keV)
Ca (3.69 keV)
Ti (4.51 keV)
Ti (4.93 keV)
Cr (5.41 keV)
Mn (5.9 keV)
Fe (6.4 keV)
Co (6.93 keV
Ni (7.48 keV)
Cu (8.05 keV)
Zn (8.64 keV)
Ga (9.25 keV)
As (10.54 keV)
Rb (13.16 keV)
Sr (14.16 keV)
Zr (14.96 keV)
Counts
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10
1
100
200
300
400
500
600
700
800
900
1000
1100
1200
Channel Number

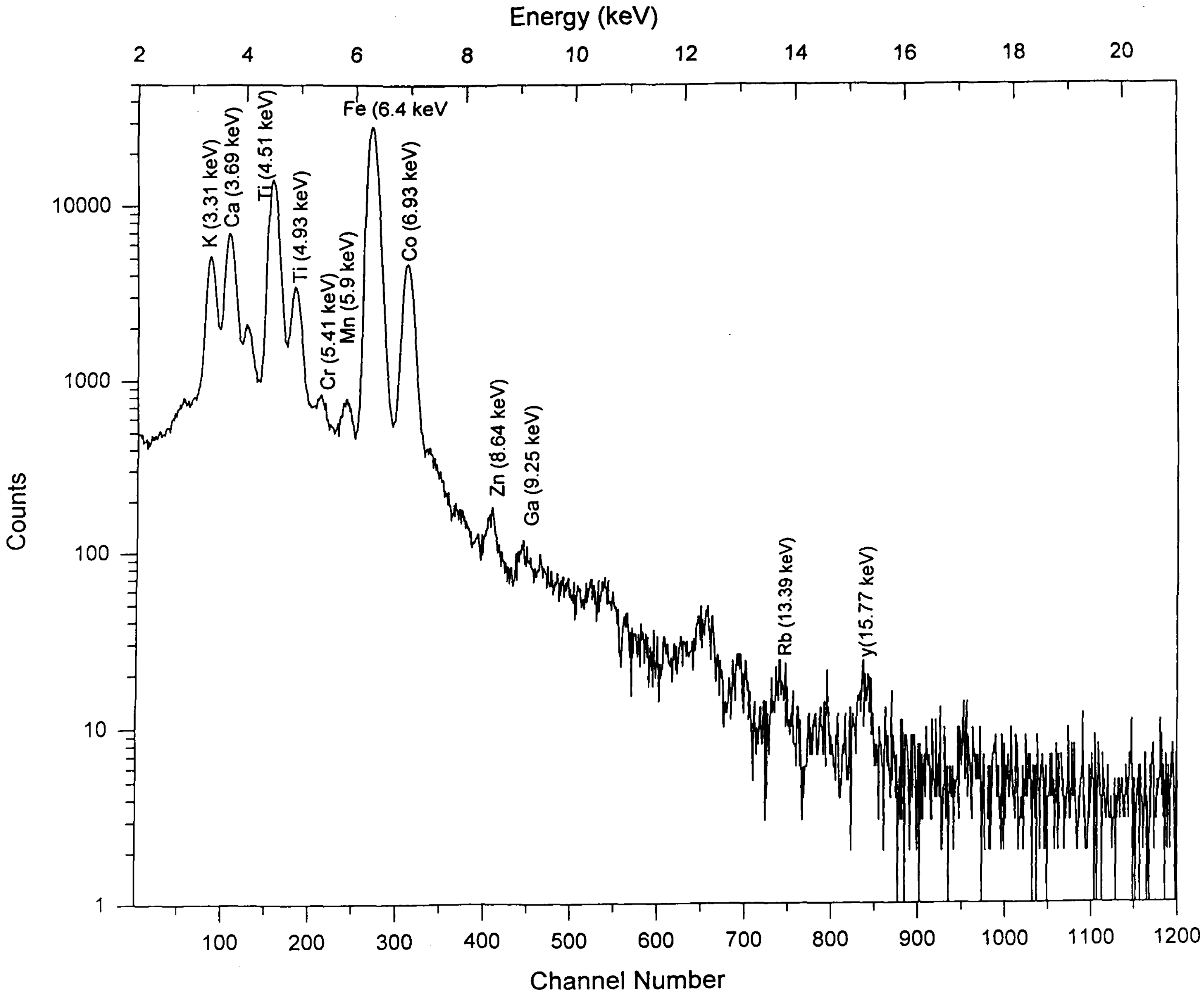

Fig. 4.3.2 Typical PIXE Spectra of Fly Ash Sample Collected from site AC2.

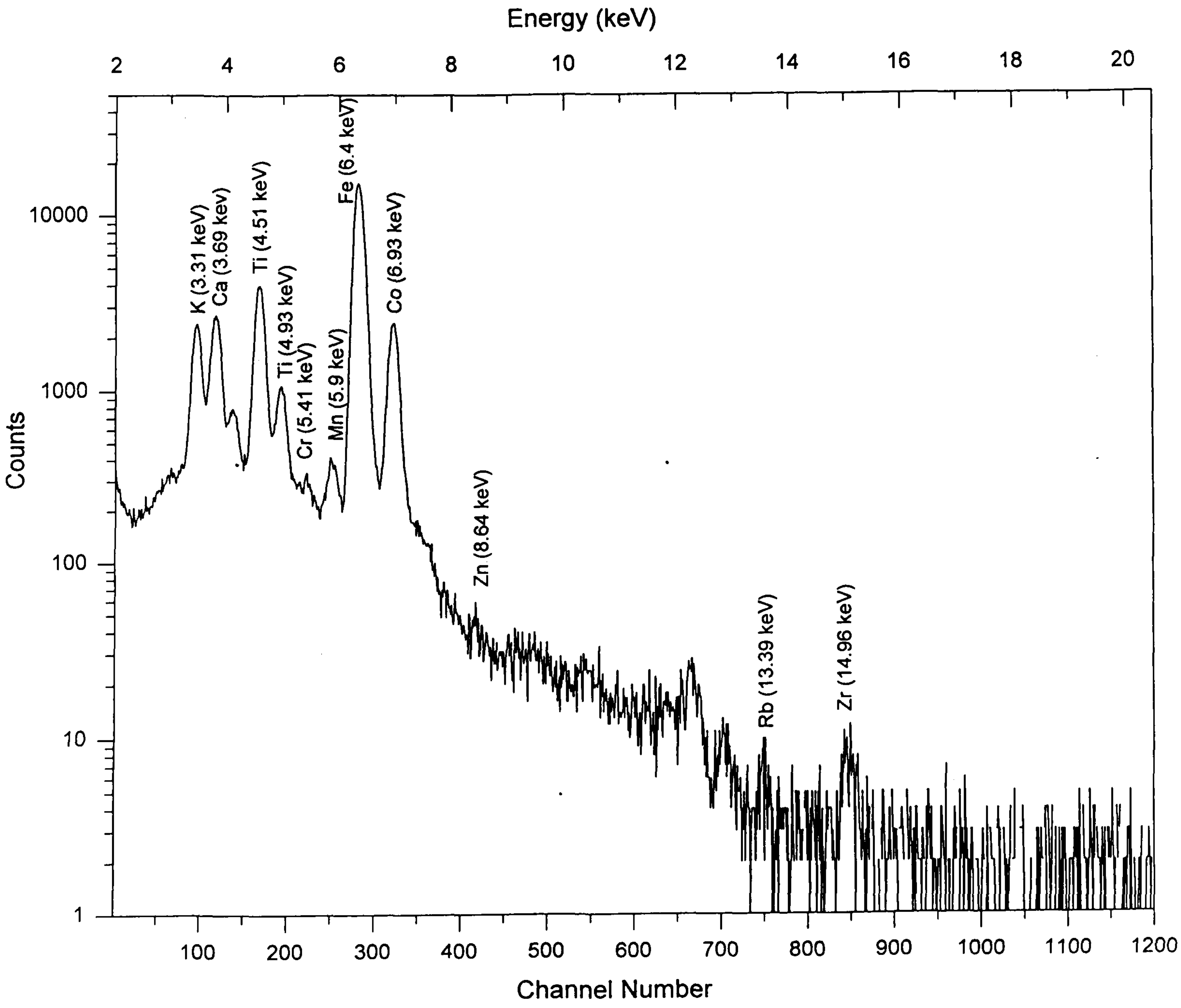

Fig. 4.3.3 Typical PIXE Spectra of Fly Ash sample Collected from Site AO3,

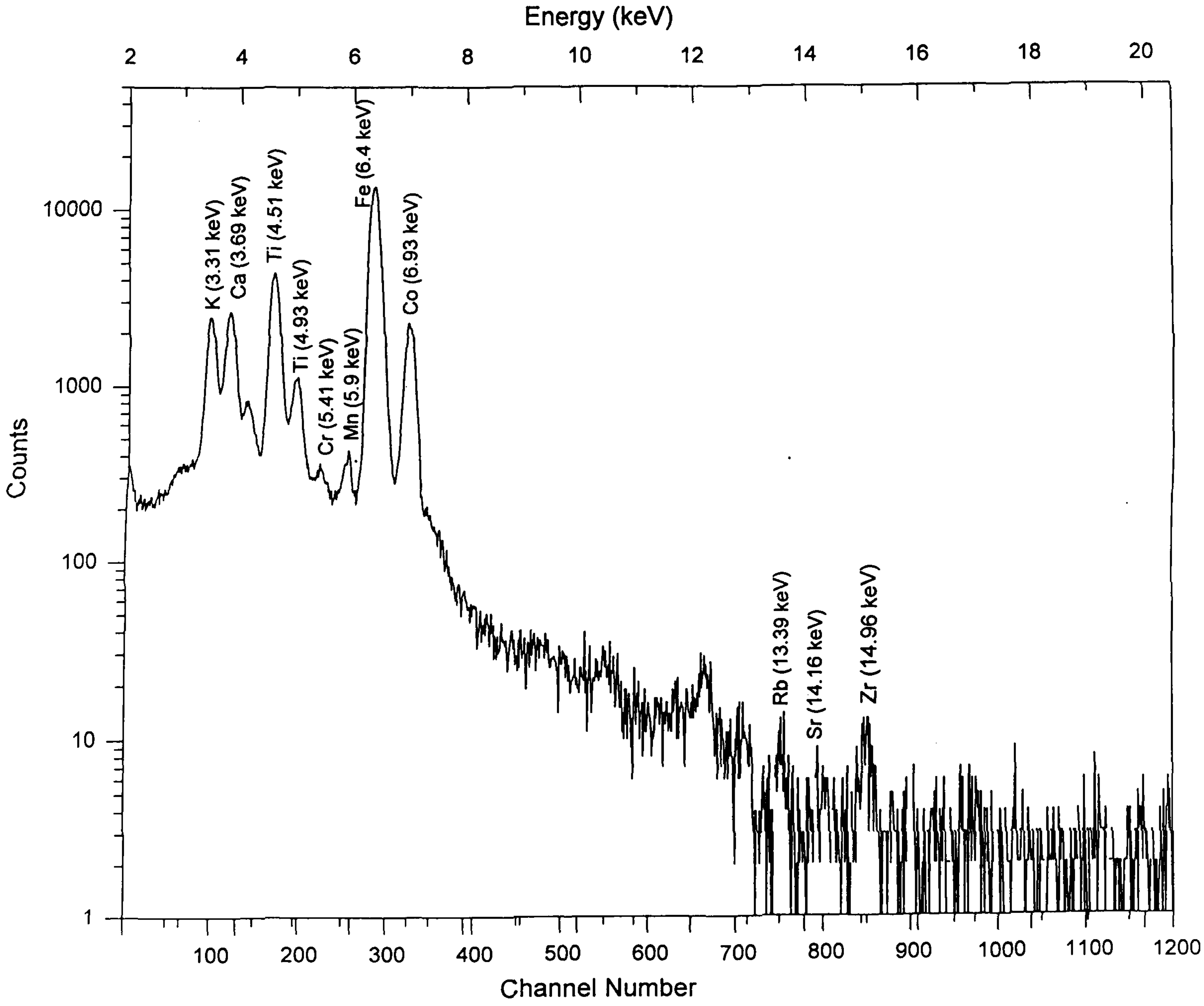

Fig. 4.3.4 Typical PIXE Spectra of Fly Ash Sample Collected from Site AO4.

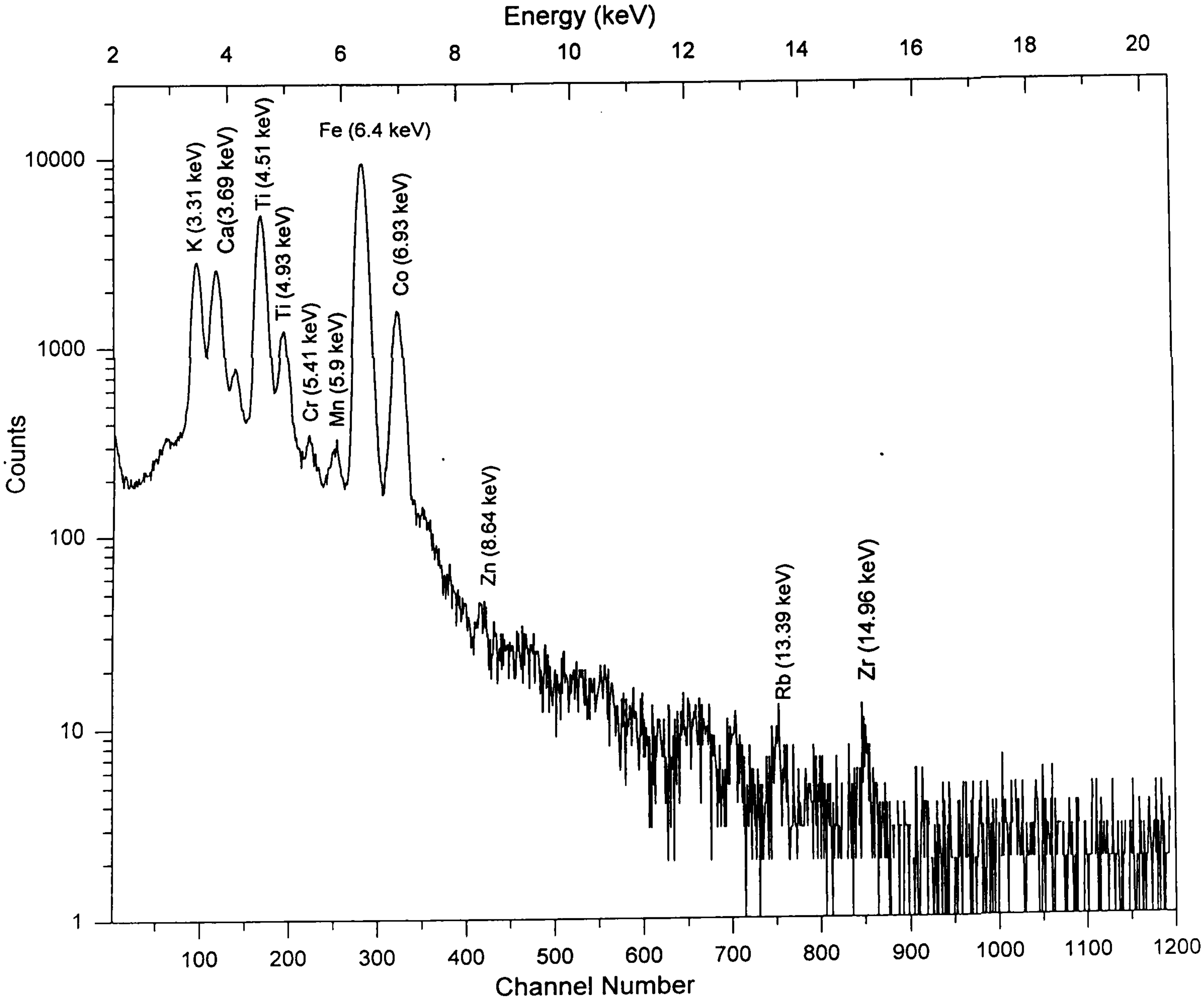

Fig.4.3.5 Typical PIXE Spectra of Fly Ash Sample Collected from Site AO5.

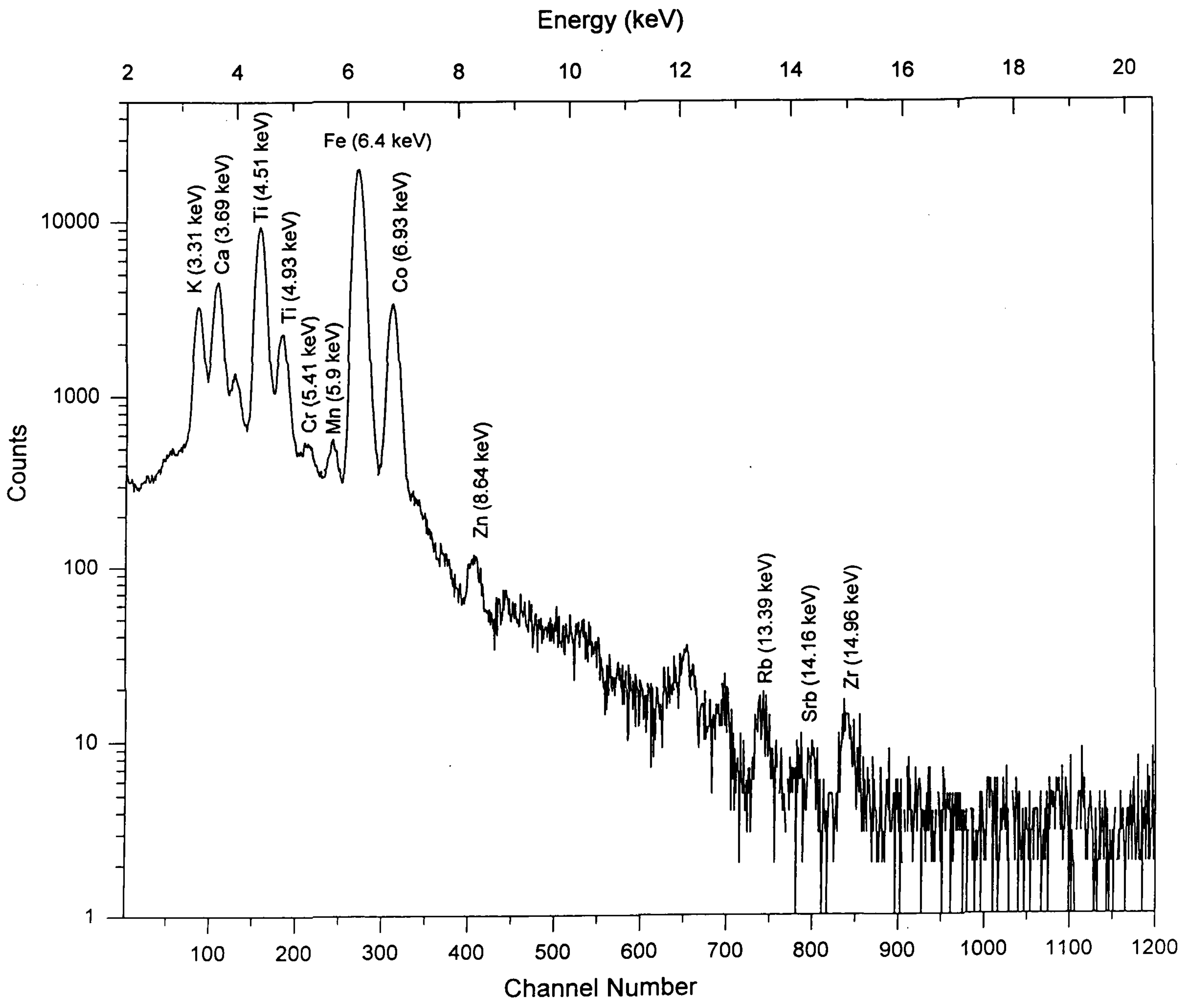

Fig. 4.3.6 Typical PIXE Spectra of Fly Ash Sample Collected from Site NTPC1.

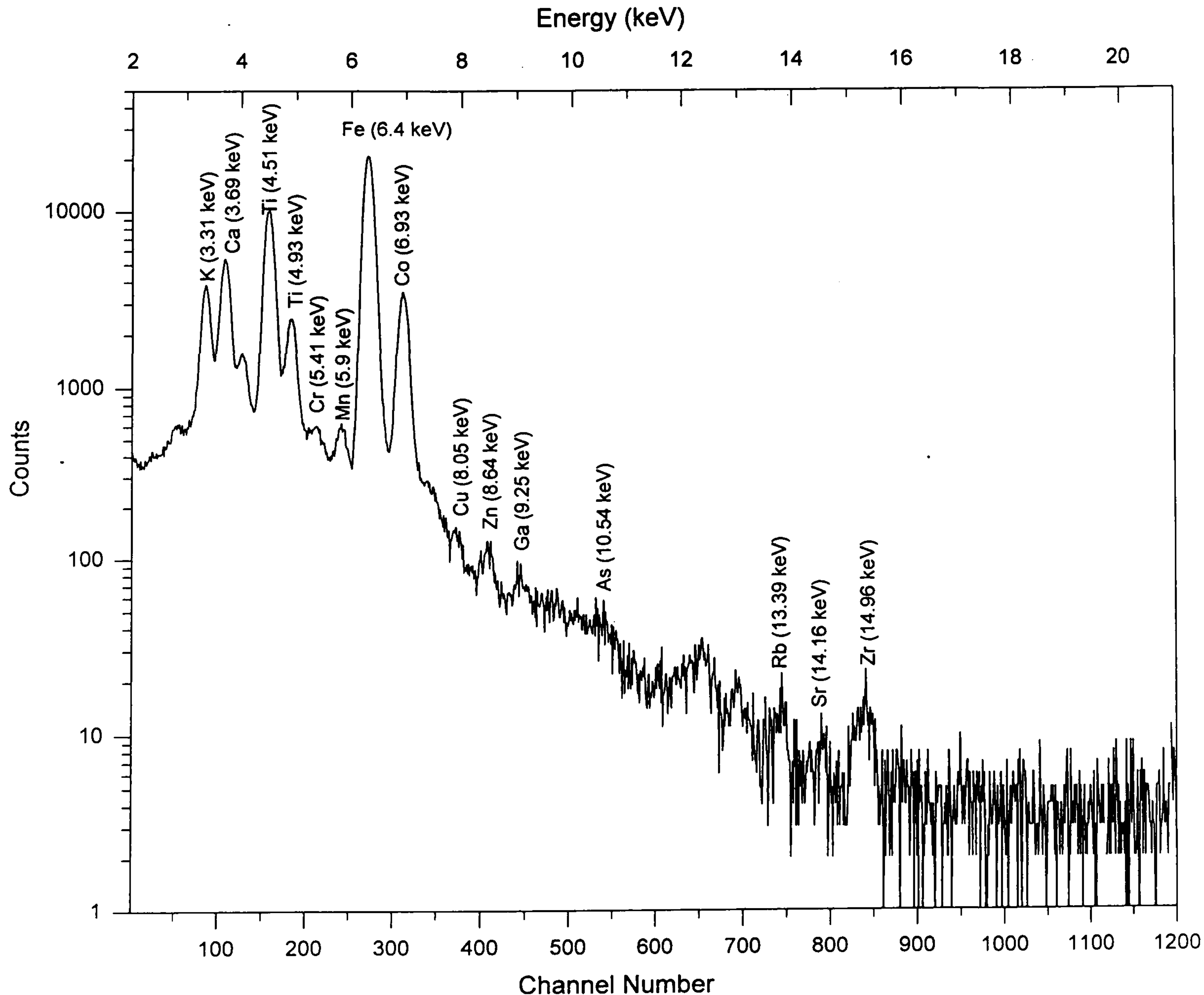

Fig. 4.3.7 Typical PIXE Spectra fo Fly Ash Sample Collected from Site NTPC2.

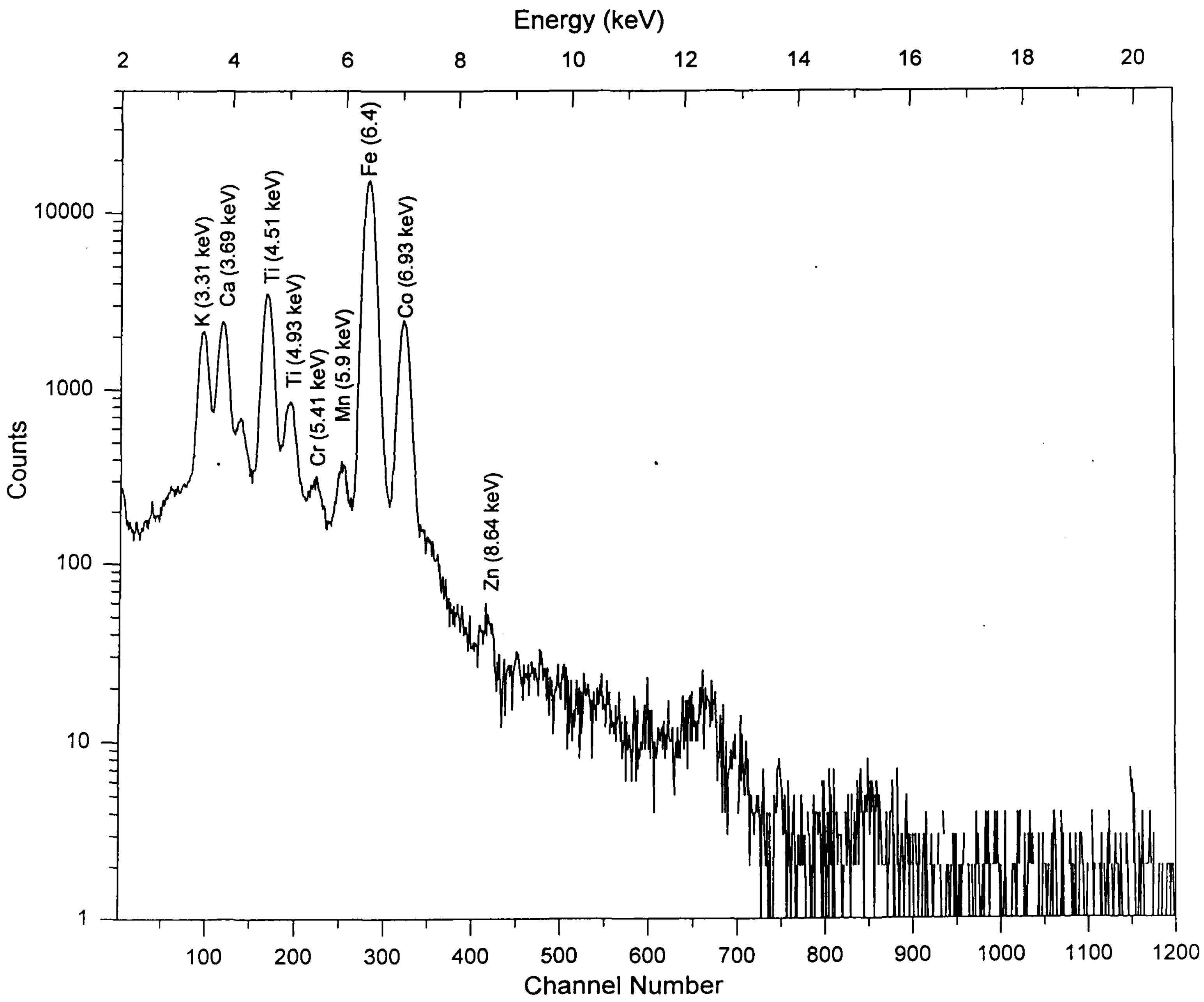

Fig. 4.3.8 Typical PIXE Spectra of Fly Ash Sample Collected from Site NTPC3.

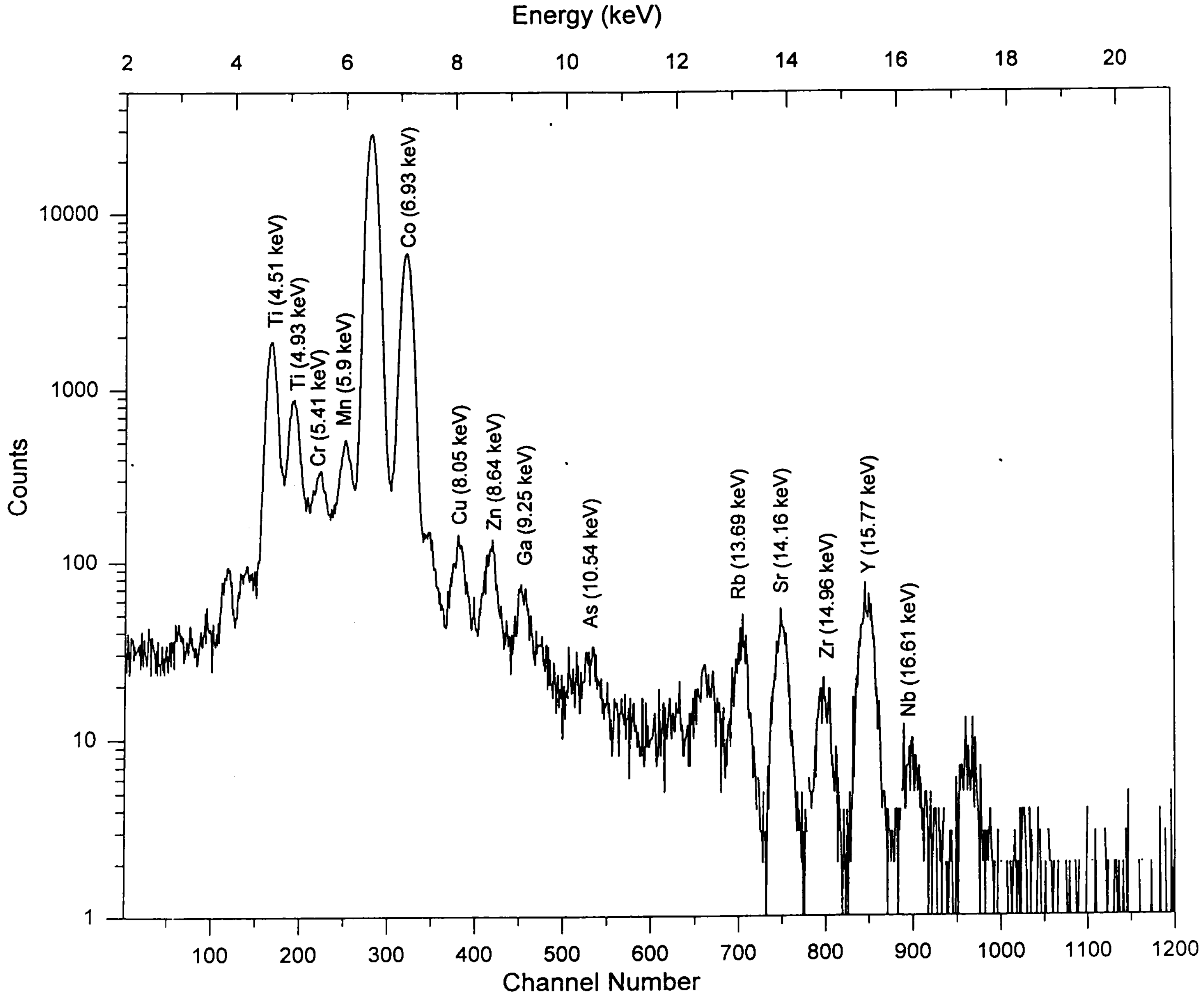

Fig. 4.3.9 Typical PIXE Spectra of Fly Ash Sample Collected from Site AC1,
With X-ray absorber of 50μm Al, 50μm Mylar and 4.2cm Air.

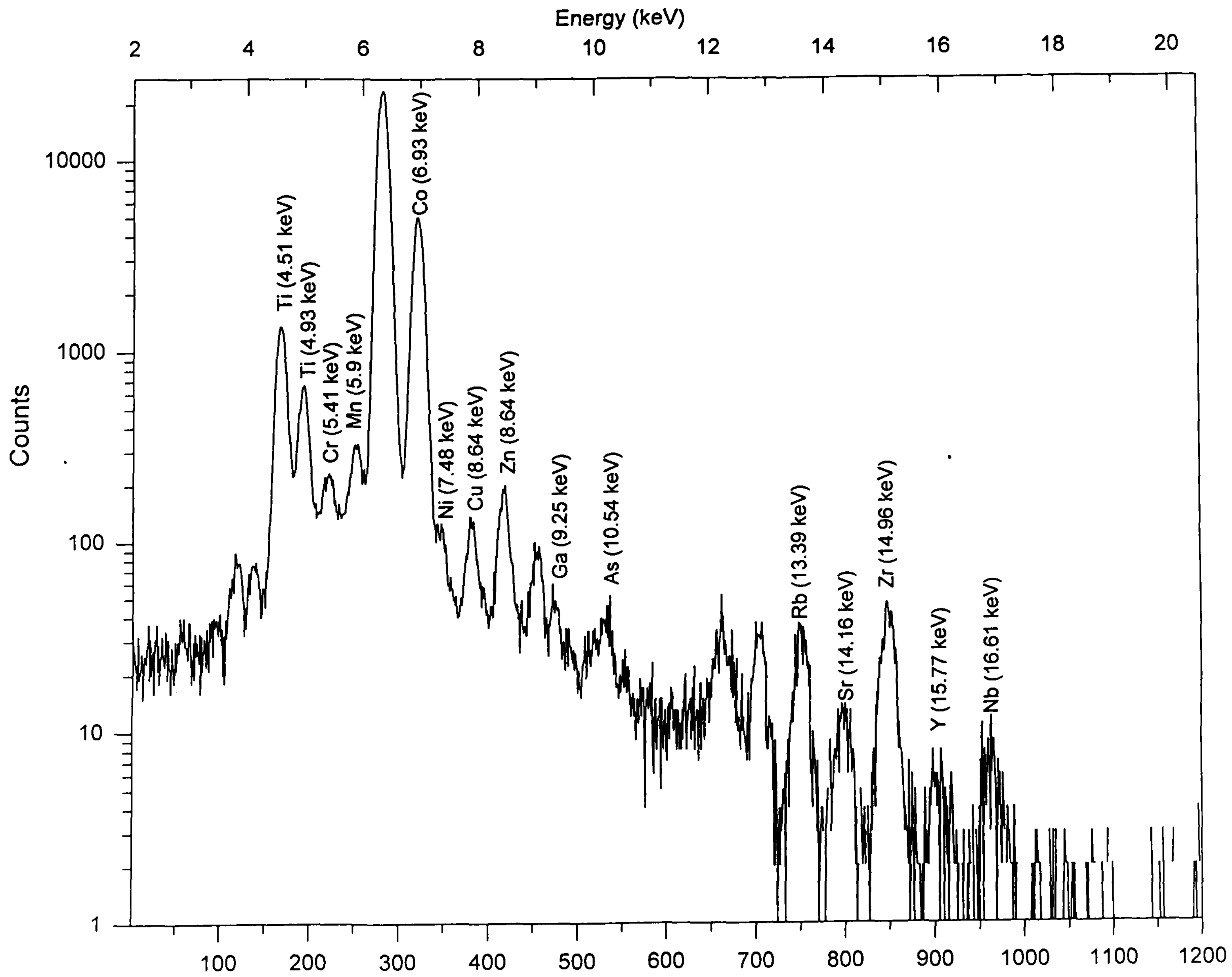

Fig. 4.3.10 Typical PIXE Spectra of Fly Ash Sample Collected From Site AC2, With X-ray absorber of 50μm Al, 50μm Mylar and 4.2cm Air.

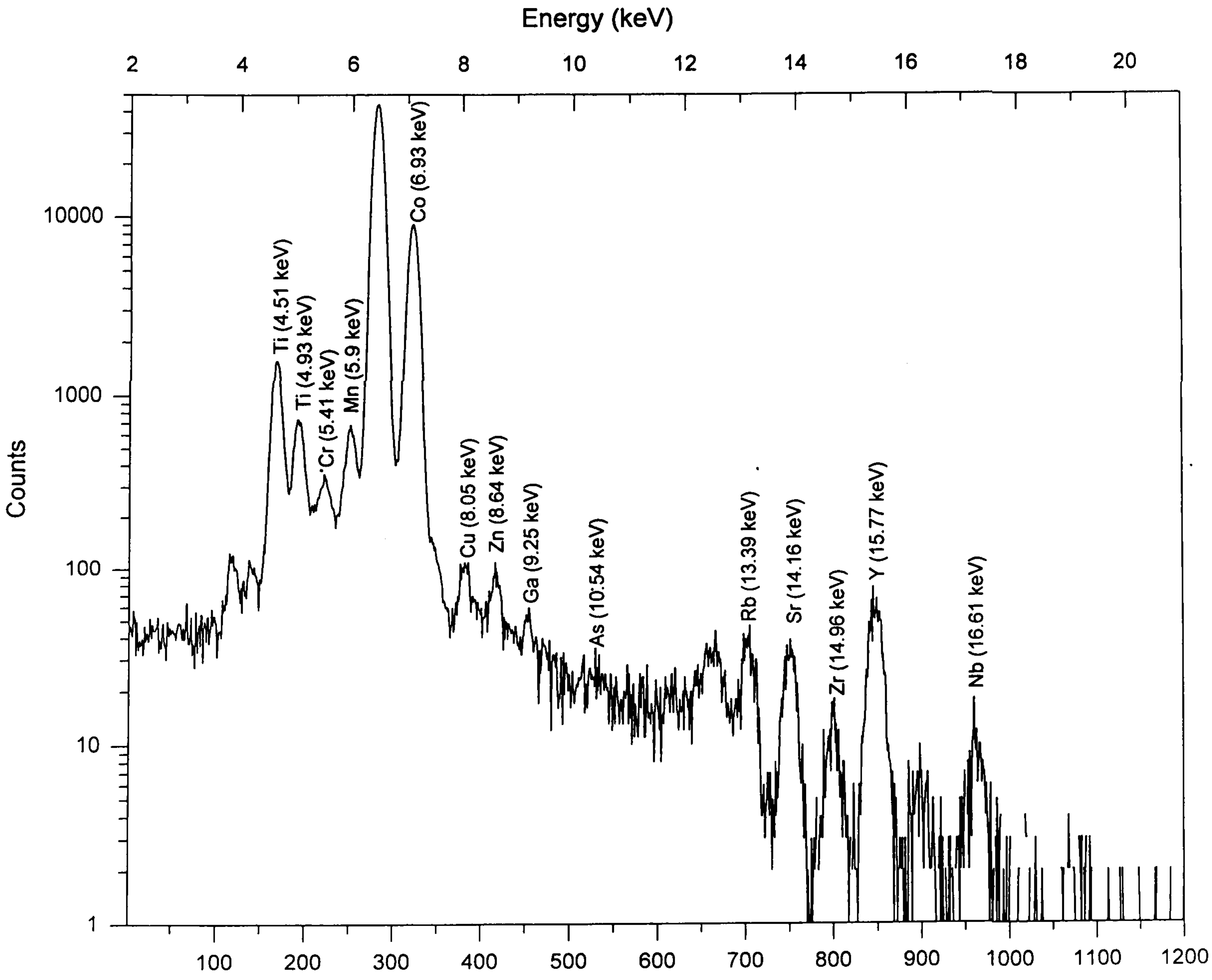

Fig. 4.3.11 Typical PIXE Spectra of Fly Ash Sample Collected from Site AO3, with X-ray absorber of 50μm Al, 50μm Mylar and 4.2cm Air.

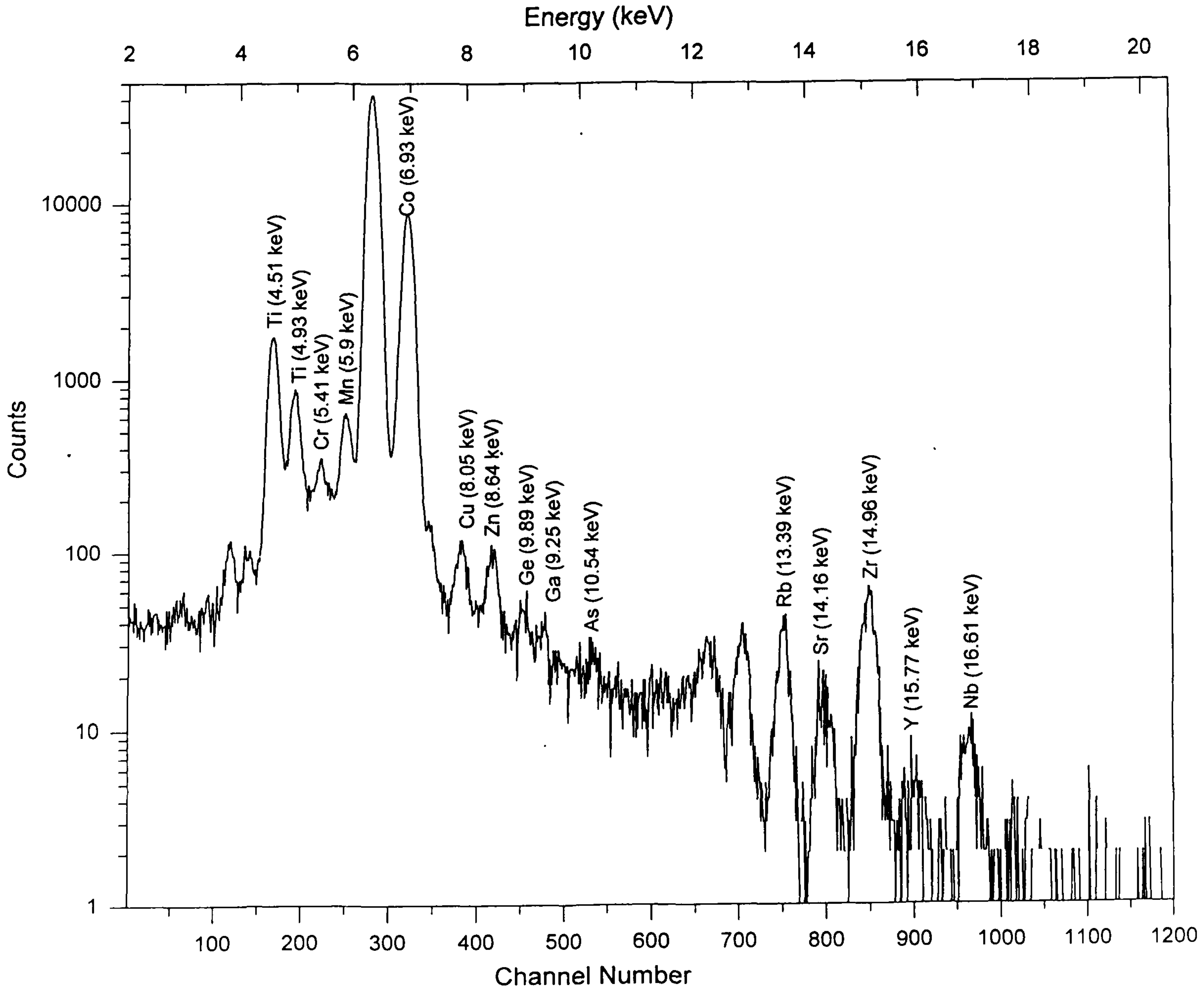

Fig.4.3.12 Typical PIXE Spectra of FLY Ash Sample collected from AO4, with X-ray absorber of 50μm Al, 50μm Mylar and 4.2cm Air.

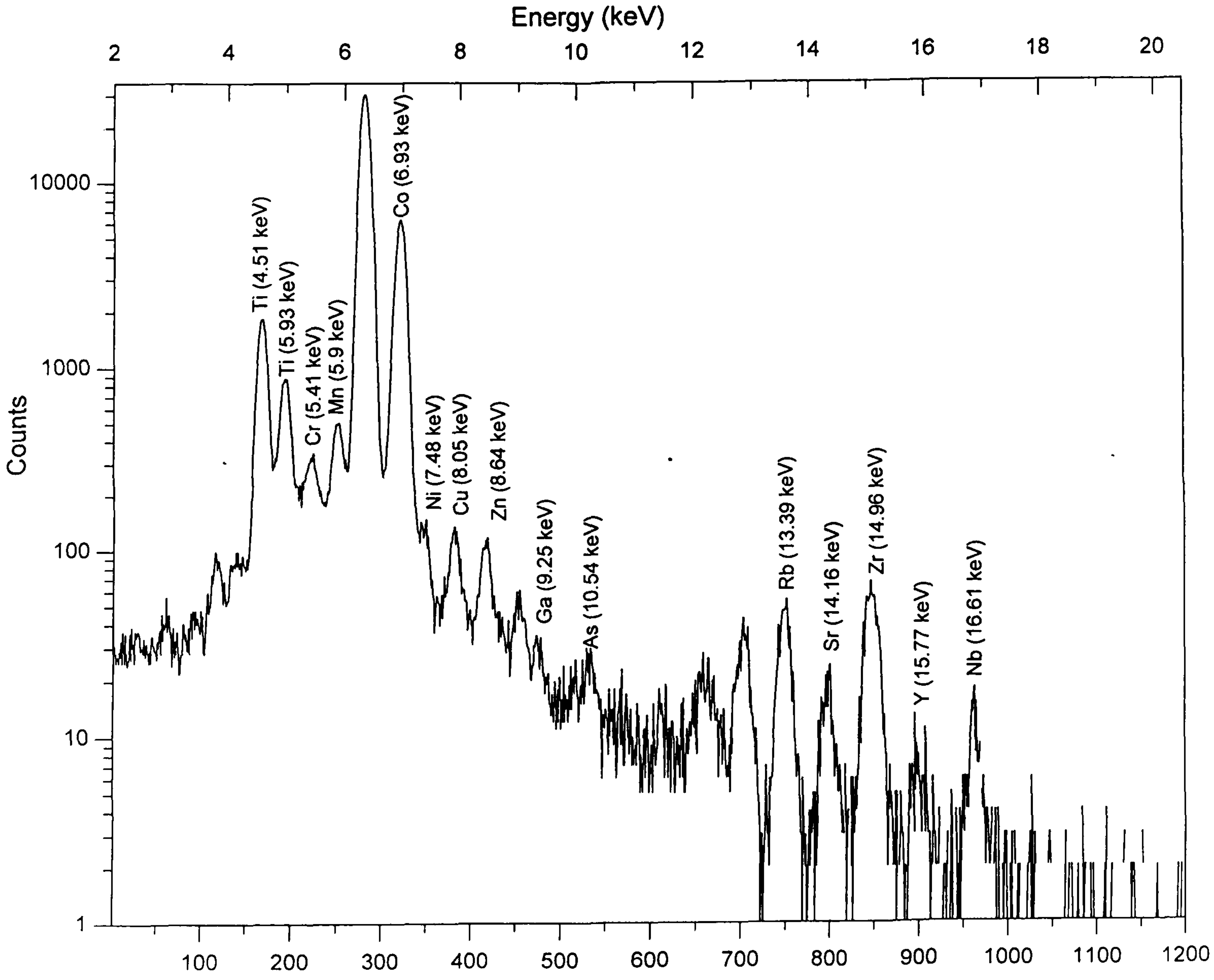

Fig. 4.3.13 Typical PIXE Spectra of Fly ASh Sample Collected fron Site AO5,
With X-ray absorber of 50µm Al, 50µm Mylar and 4.2cm Air.

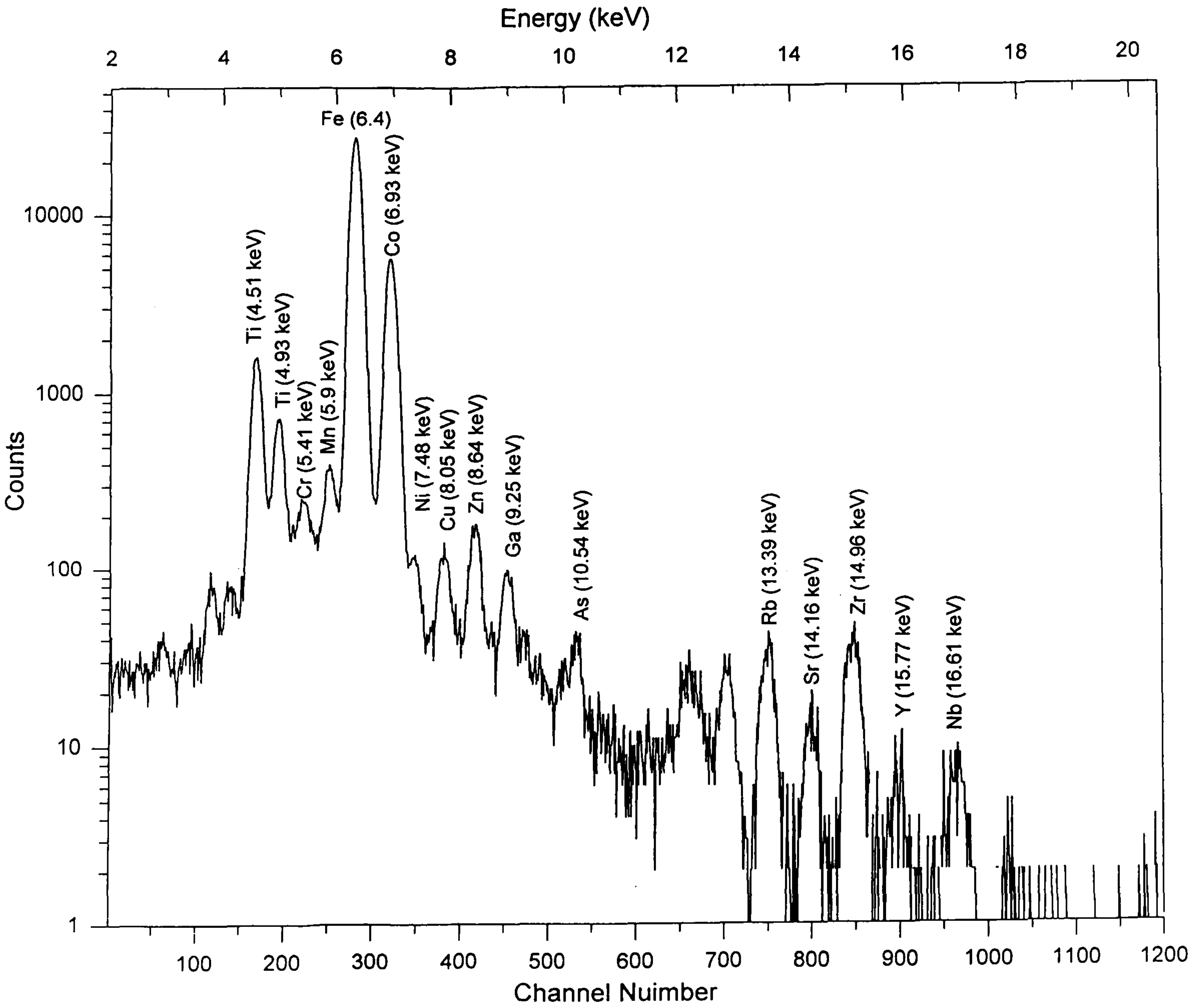

Fig. 4.3.14 Typical PIXE Spectra of Fly Ash Sample Colllected form Site NTPC1, With X-rav absorber of 50μm Al. 50μm mylar and 4.2cm Air.

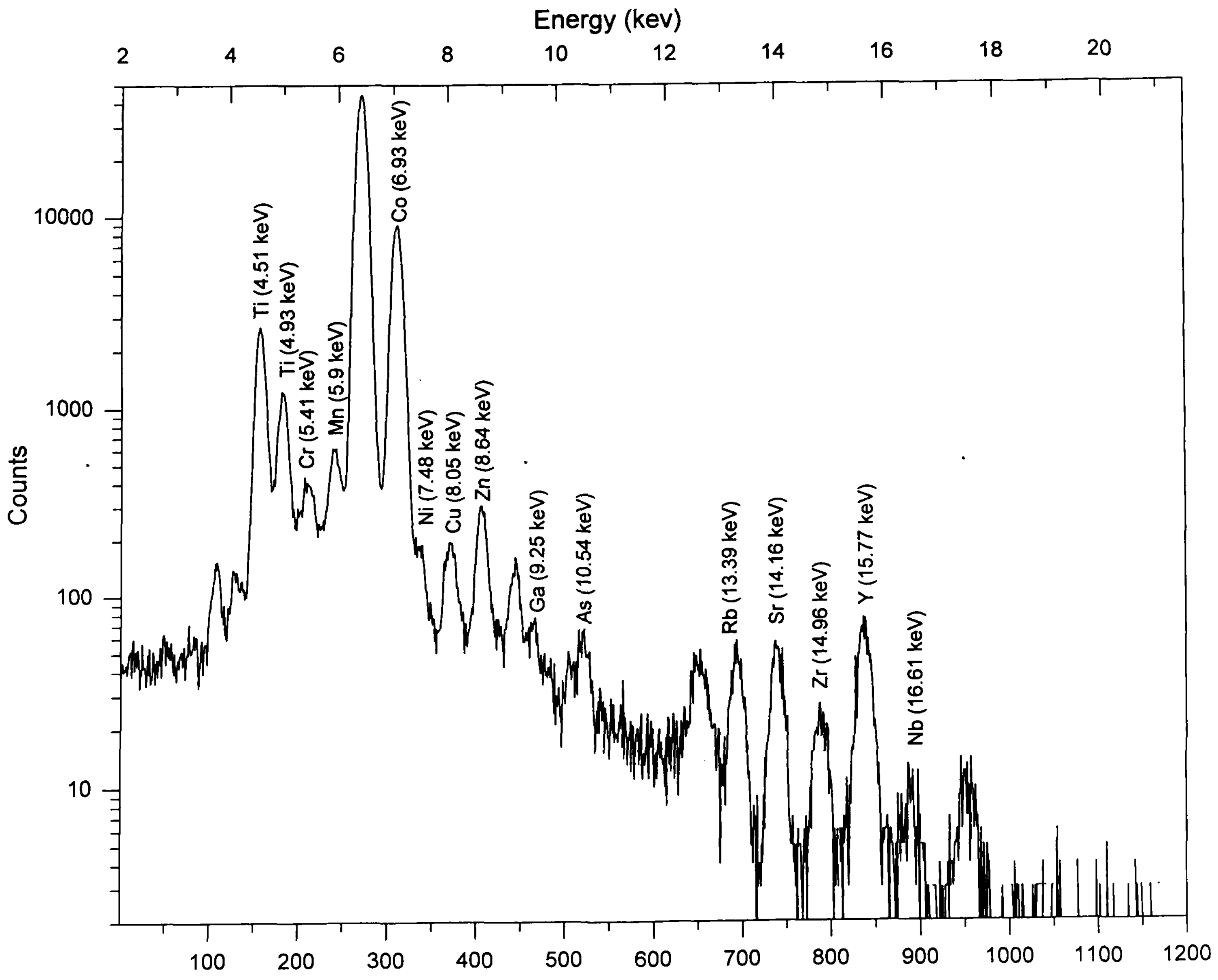

Fig. 4.3.15 Typical PIXE Spectrum of Fly Ash Sample Collected from Site NTPC2, With X-ray absorber of 50μm Al, 50μm Mylar and 4.2cm Air.

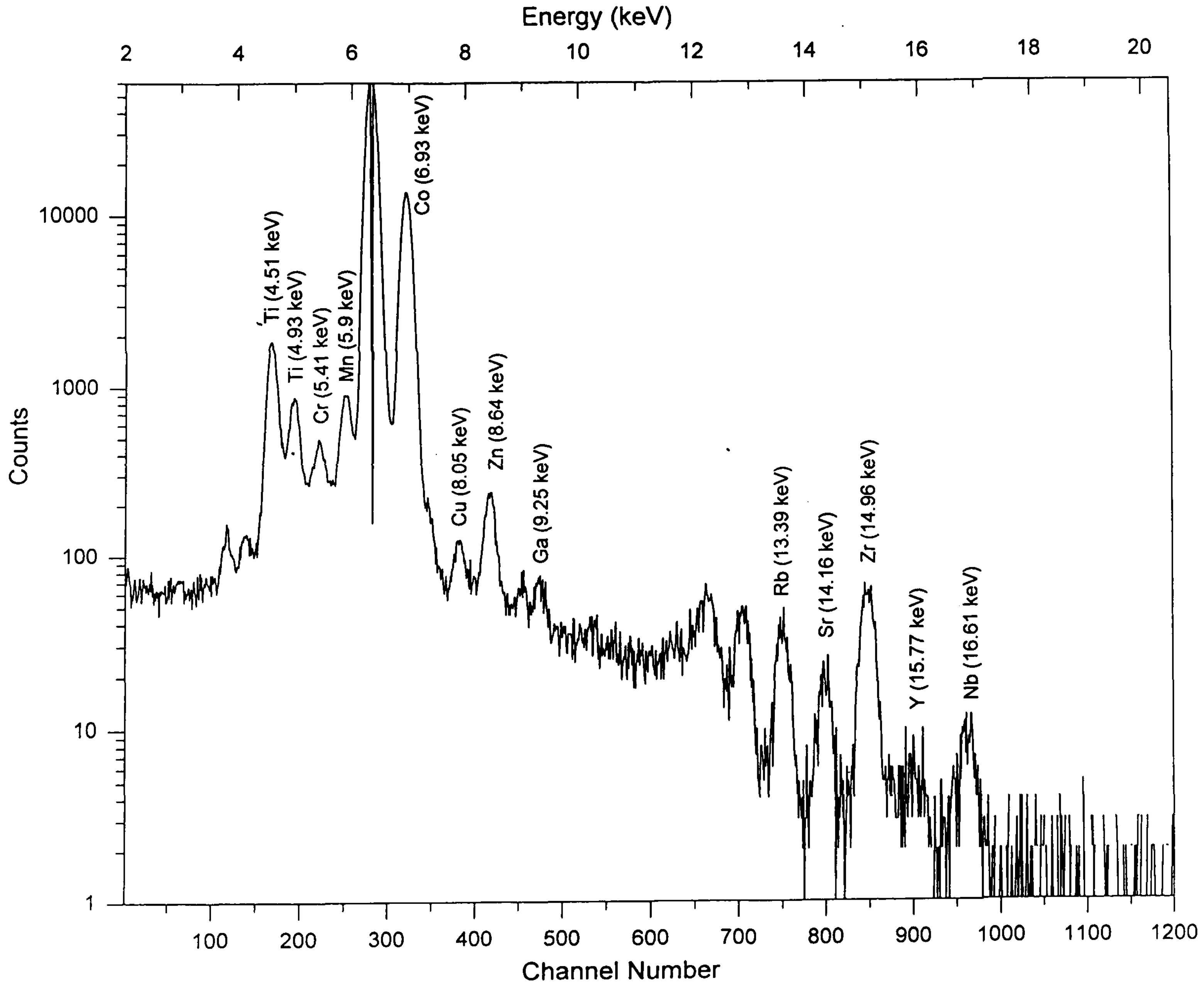

Fig. 4.3.16 Typical PIXE Spectra of Fly Ash Sample Collected from Site NTPC3, with X-ray absorber of 50μm Al, 50μm Mylar and 4.2cm Air.

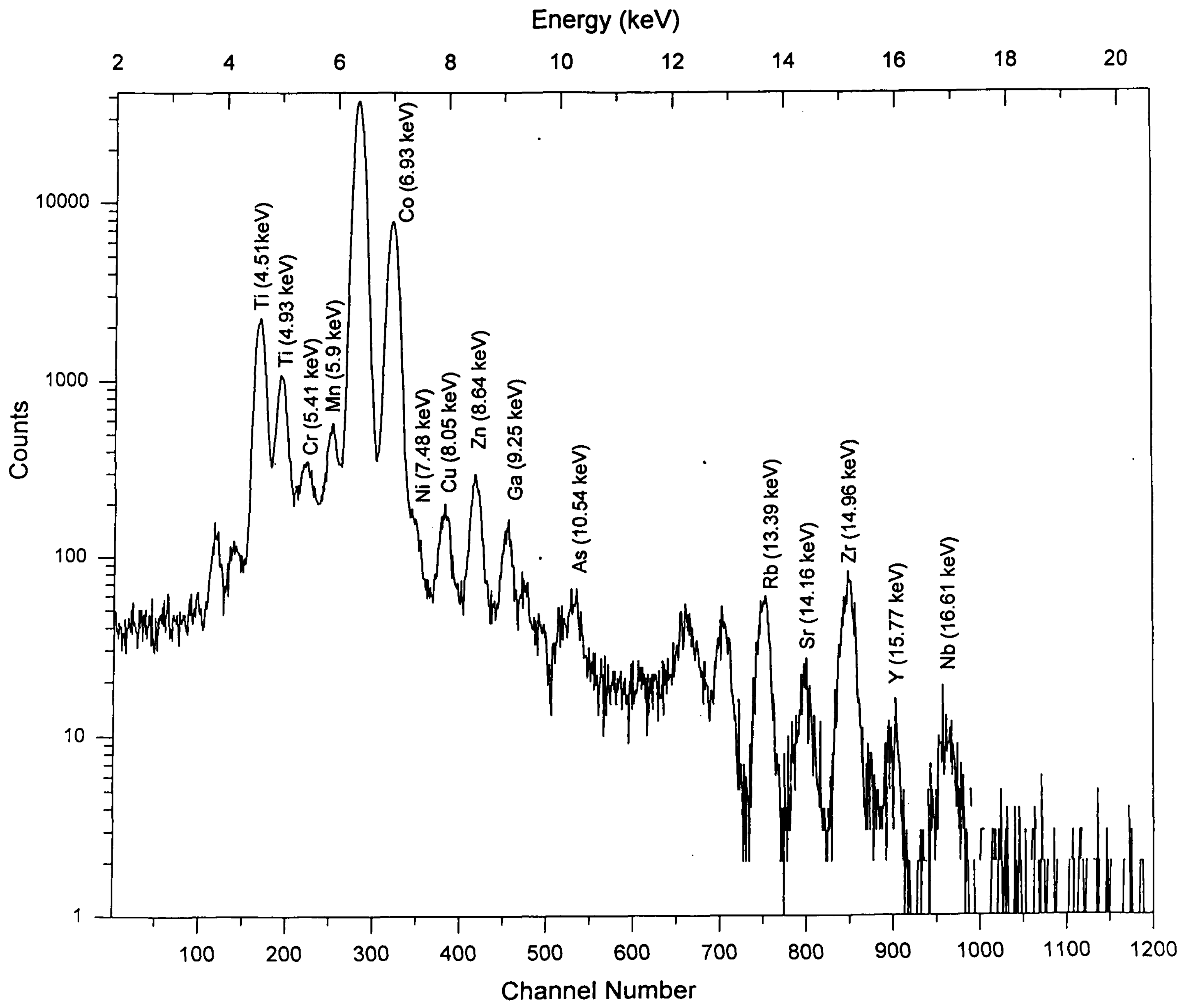

Fig. 4.3.17 Typical PIXE Spectra of Fly Ash Sample Collected from Site NTPC4, with X-ray Absorber of 50μm Al, 50μm Mylar and 4.2cm Air.

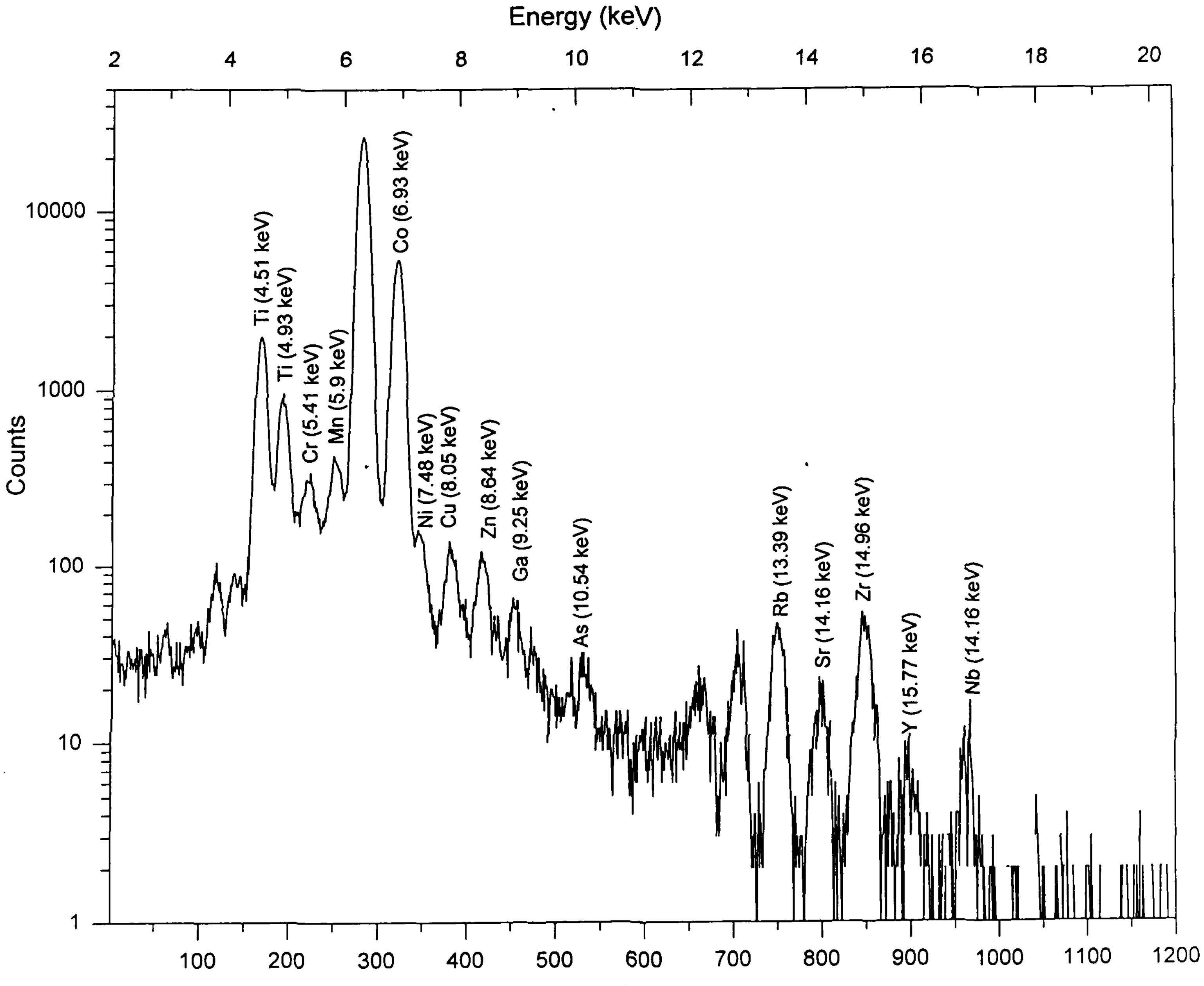

Fig. 4.3.18 Typical PIXE Spectra of Fly Ash Sample Collected from Site PANKI 1, *with X-ray absorber of 50μm Al, 50μm* Mylar and 4.2cm Air.

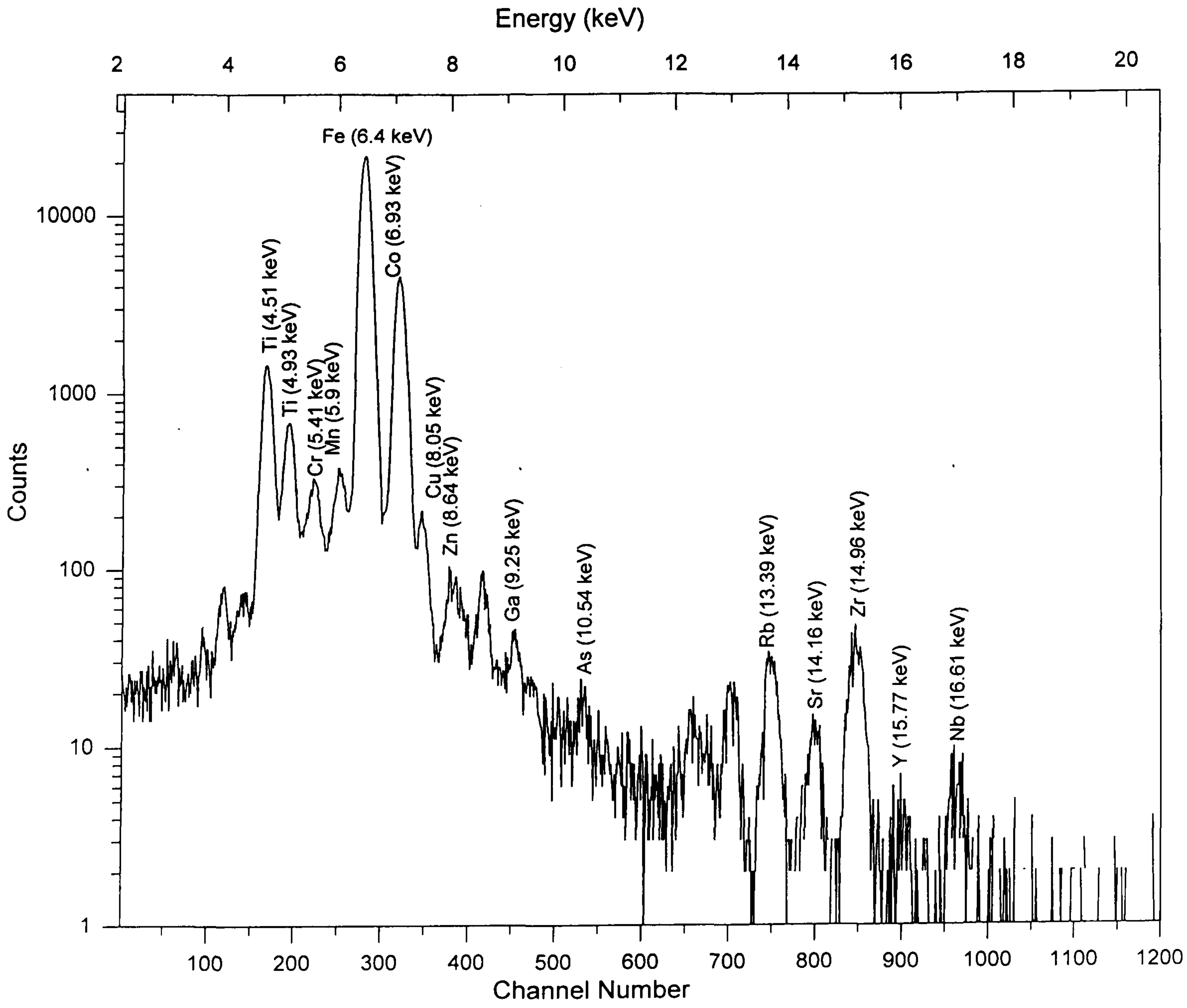

Fig. 4.3.19 Typical PIXE Spectra of Fly Ash Sample Collected from Site PANKI 2, with X-ray absorber of 50μm Al, 50μm Mylar and 4.2cm Air.

such, in the spectra of Figs. 4.3.18 and 4.3.19, the peak at energy 3.31 keV corresponding to potassium K_α X-ray could not be observed in the spectrum.

4.4 Analysis

The GUPIX Software [1] has been used for the analysis of PIXE spectra. GUPIX is a multi elemental analysis program intended to analyse an ion induced energy dispersive X-ray spectrum from thin, intermediate, thick or multi layered targets, in order to determine the element concentrations. The intensities of the characteristic X-ray peaks are determined by fitting a model spectrum to the measured spectra.

The model spectrum is generated by using Gaussian peaks for each of the main X-ray lines for the element chosen. A library of the peak energies and intensities relative to the main peak for that element is used to reduce the number of parameters from one per peak to one per element. In order to do this it is necessary to have an extensive database of X-ray energies, X-ray production cross-sections, X-ray attenuation coefficients, proton stopping power, elemental densities and atomic weights etc. This data base is provided in the computer code GUPIX.

The code consists of two separate sections, a data input section coupled to a fitting procedure and an output section, each of which calls many subroutines. GUPIX uses the method of non linear least square fitting followed by an integrated linear least square method which is used to fit a PIXE spectrum of up to 2048 channels containing the X-ray peaks of a maximum of 60 elements. Lorentzian width and relative intensities, proton induced ionization cross-sections which when combined with fluorescence yields and Coster-Kroning transition probabilities provide the necessary X-ray production cross-section, are inbuilt in the programme. Element density, atomic weight, and photoelectric cross-section make it possible to compute secondary fluorescence contributions to the spectrum. Use of this data base alongwith various numerical procedures make it possible to describe a PIXE spectrum through the linear least square method. The software arrives at accurate estimates of the number of X-ray events due to each element that are present in the spectrum produced by the bombarding thin, thick and multilayered targets with the proton beam of known energy. Calibration factor and charge used for the obtaining concentrations from peak intensities depend on the instrumental constant. The relative charge collected for the run must be known in order to convert peak area to elemental concentrations in the order of ppm.

The X-ray Spectra of coal fly ash sample obtained from the National Institute for Standard and Technology (NIST) [2] without and with absorber are shown in Figs 4.3.20 and 4.3.21 respectively. From these spectra it is clear that there are sharp and clear peaks, mainly in the transition element region. For low atomic number region, i.e., Z<13 there is large self-absorption of low energy X-rays within the sample itself, due to which the sensitivity is low.

In the analysis of PIXE spectra of the samples taken from Harduaganj thermal power plant Aligarh, the elements K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, and Pb etc, were detected.

In samples taken from the national thermal power plant, Dadri, Ghaziabad, elements K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, and Pb etc, were found. In samples taken from the Panki thermal power plant,

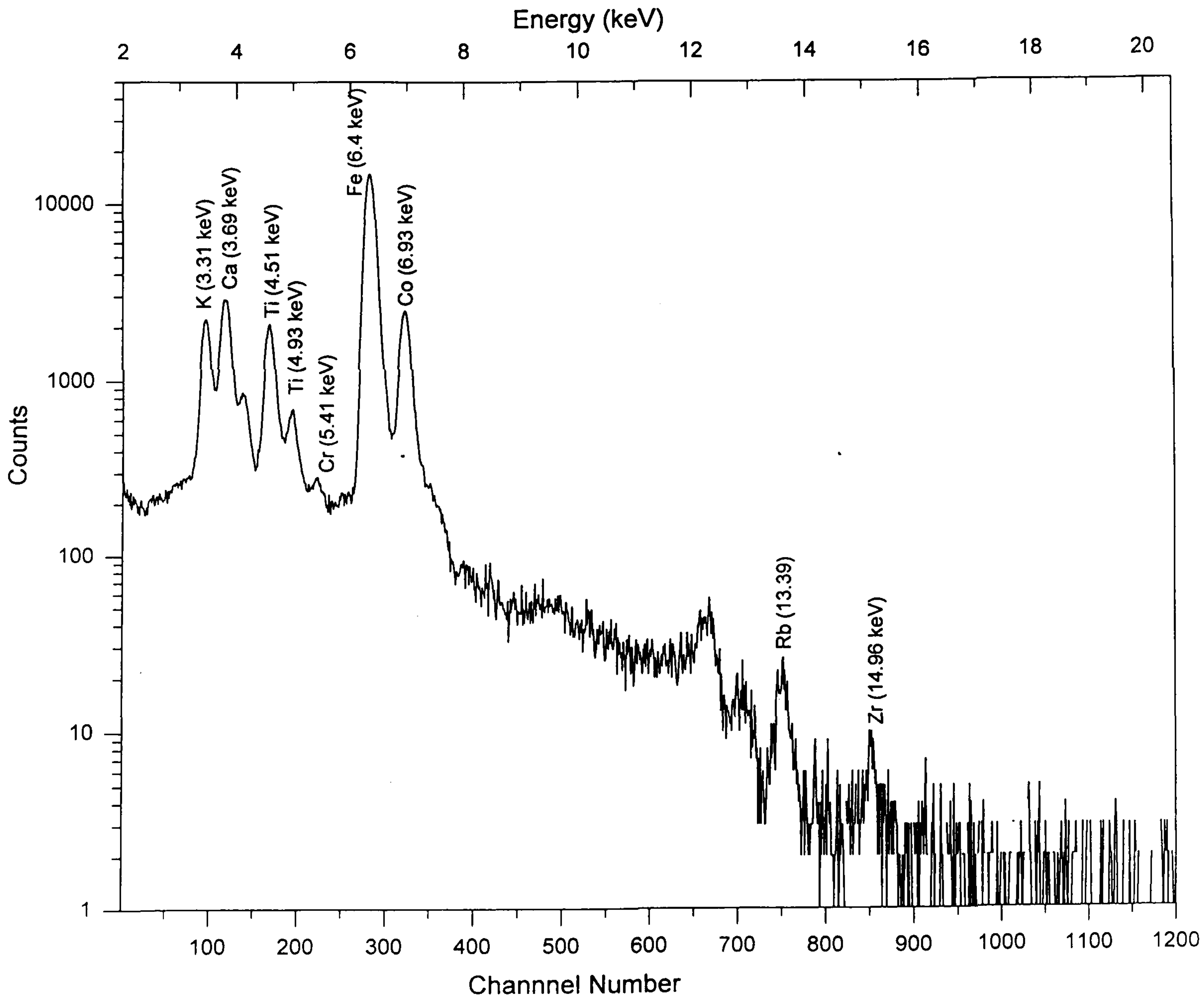

Fig.4.3.20 Typical PIXE Spectra of Standard Coal coal Fly Ash Obtained from NIST.

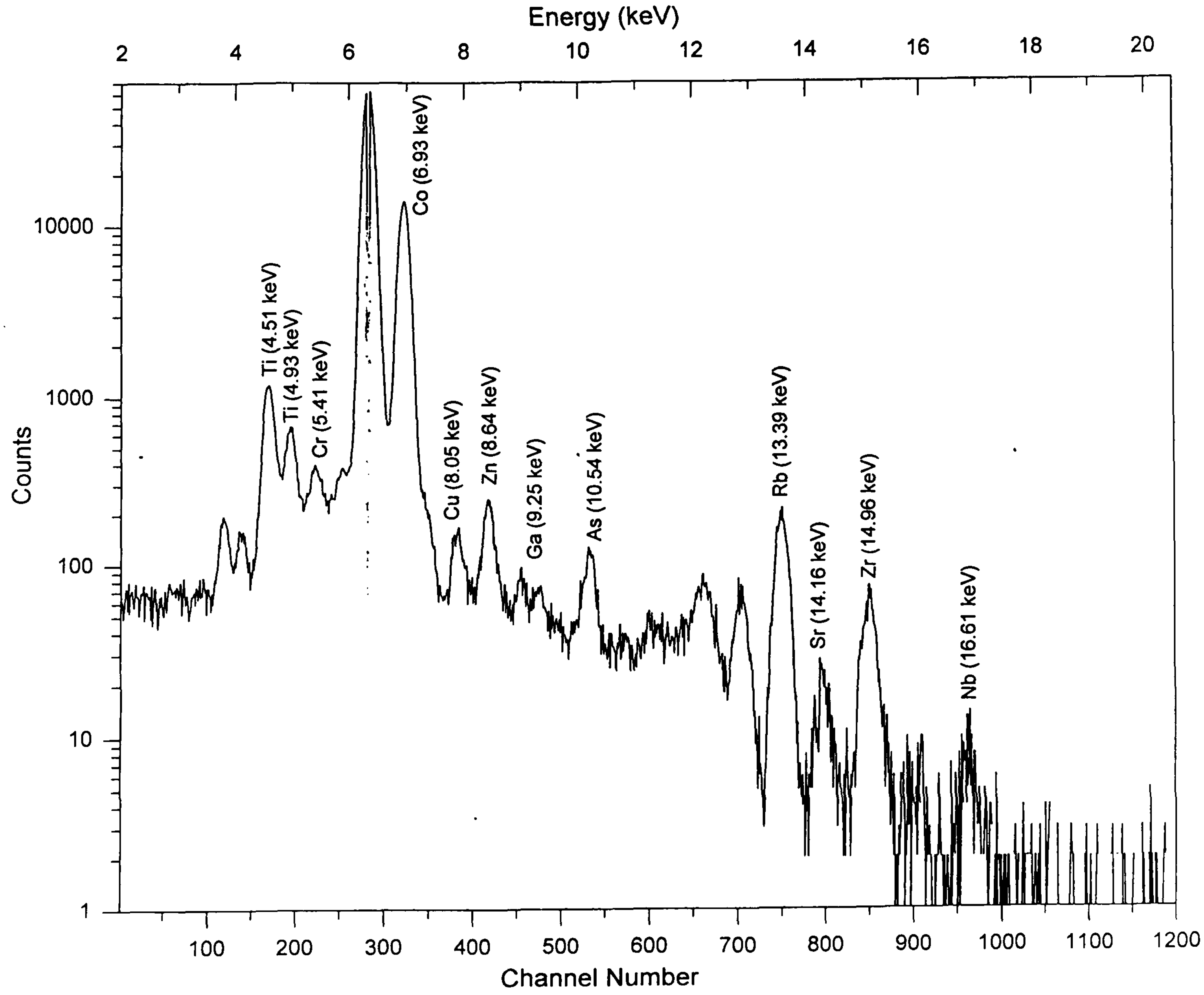

Fig. 4.3.21 Typical PIXE Spectra of Standard Fly Ash, with X-ray absorber of 50μm Al, 50μm Mylar and 4.2cm Air.

Kanpur, the peaks due to elements Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, and Pb etc, were observed. On comparing the results of these thermal power plants it is found that about 18 trace elements are present in the coal fly ash sample of National thermal power plant and Harduaganj thermal power plant, and about 15 trace elements are present in the coal fly ash samples taken from Panki thermal power plant, Kanpur.

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CHAPTER V

Results and Discussion

The PIXE analysis of eleven specimens of fly ash samples collected from three different thermal power plants has been performed. In Table 5.1, the results of PIXE analysed values of the NIST coal fly ash standard reference material are given alongwith the certified values. As can be seen from the comparison of the two, the results are very close to each other, which gives us a confidence in the analysis procedure. In the present work as, expected a high percentage of iron, manganese, titanium and calcium have been found in all fly ash samples in general. Among toxic elements there is a considerable quantity of Cr, Zn, Pb, As, and Ni in all the fly ash samples, which is quiet alarming from the public health point of view, particularly because of the fact that the fly ash is also being used by farmers, ceramics and brick manufacturers.

The elemental composition of the fly ash samples from Harduaganj Thermal Power Station (HTPS) Aligarh is given in Table 5.2. Eighteen elements viz., K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, and Pb etc, have been detected using PIXE. The elemental composition for the coal fly ash sample from the National Thermal Power Plant, Dadri, Ghaziabad, is given in Table 5.3, where again all the above elements could be detected. In the fly ash samples of HTPS (Aligarh) and National Thermal Power Corporation (NTPC) Dadri, 18 elements could be detected. The elemental composition for the samples from the Panki thermal power plant, Kanpur, is given in Table 5.4 and is found to have all the elements as in case of other two plants except K, Ge, and Nb. In all 15 elements are found to be present in them. It may be pointed out that the reason for the absence of K in Table 5.4 is already given in Chapter 4.

Table: 5.1 Elemental profile in NIST Coal Fly Ash Standard Reference Materials.

Element	PIXE Analysed values	Certified values
K (%)	1.91± 0.02	1.95± 0.03
Ca (%)	1.52 ± 0.01	1.51± 0.06
Ti (%)	0.812± 0.007	0.791± 0.014
Cr	245.4 ± 23.1	198.2 ± 4.7
Mn	114.8± 19.4	131.8 ± 1.7
Fe(%)	7.742 ± 0.007	7.78 ± 0.23
Ni	100.4 ± 11.0	120.6 ± 1.8
Cu	120.6 ± 5.7	112.8 ± 2.6
Zn	224.6 ± 6.5	210 *
Ga	58.5 ± 5.4	-------
As	157.5 ± 7.4	136.2 ± 2.6
Rb	199.4 ± 10.6	140 *
Sr	1089.3 ± 20.7	1041± 14
Y	65 ± 11.5	-------
Zr	282.7 ± 23.2	-------
Pb	63.7 ± .2	68.2 ± 1.1

* Non- certified value

Table 5.2: Trace element concentrations in the fly ash samples from HTPS, Aligarh

Sample ID⇒	AO 3	AO 4	AO 5	AC 1	AC 2
Elements	Conc.	Conc.	Conc.	Conc.	Conc.
K (%)	0.5154 ± 0.004	0.4591 ± 0.004	------	1.2320 ± .085	0.8561 ± .059
Ca (%)	0.897 ± 0.074	0.8397 ± .077	0.6407 ± .047	0.5448 ± .006	0.7318 ± .005
Ti (%)	1.019± 0.011	1.1737 ± .011	1.2480 ± .011	1.1875 ± .004	1.2676 ± .003
Cr	193.2 ± .0016	154.6 ± 16.2	192.7 ± 15.4	196.2 ± 15.3	180.3 ± 17.3
Mn	480.6 ± 14.9	451.6 ± 14.5	351.6 ± 12.7	332.5 ± 12.6	268.2 ± 14.2
Fe (%)	4.074 ± 0.004	3.9638 ± .003	2.8116 ± 0.005	2.6865± 0.005	938 ± 0.005
Ni	46.8 ± 6.5	39 ± 6.2	61 ± 5.4	61.1 ± 5.7	54.8 ± 7.3
Cu	56.6 ± 3.9	62.2 ± 3.9	77.9 ± 3.9	82 ± 4.1	109.1 ± 5.1
Zn	51.6 ± 3.7	72.1 ± 3.6	76.8 ± 3.6	87.8 ± 4.0	200.5 ± 5.8
Ga	24.3 ± 3.4	24.7 ± 3.3	37.4 ± 3.1	51.2 ± 3.6	98.3 ± 5.1
Ge	------	-------	-------	-------	13.2 ± 4.2
As	------	14.8 ± 3.4	18.6 ± 3.2	23.7 ± 3.5	42.3 ± 5.3
Rb	86.7 ± 6.7	80.4 ± 5.9	96 ± 6.0	92 ± 6.3	118.3 ± 7.6
Sr	138.1± 7.7	156.3 ± 8.0	202.7 ± 8.9	187.9 ± 8.5	177.5 ± 10.7
Y	36.8 ± 7.0	47.5 ± 8.1	61.4 ± 7.9	60.4 ± 8.0	36.1 ± 9.3
Zr	390 ± 16.8	340.2 ± 15.6	386.9 ± 16.2	378.4 ± 16.6	337.4 ± 18.6
Nb	36.6 ± 8.3	-------	42 ± 8.5	48.8 ± 9.1	30.3 ± 10.6
Pb	-------	11.1 ± 2.2	-------	16.7 ± 2.2	-------

Table 5.3: Trace element concentrations in the fly ash samples from NTPC, Dadri,Ghaziabad.

Sample ID ⇒	NTPC 1	NTPC 2	NTPC 3	NTPC 4
Elements	Conc.	Conc.	Conc.	Conc.
K (%)	0.4377 ± 0.0035	0.4258 ±0 .0034	1.2775 ± 0.010	-------
Ca (%)	0.3792 ± 0.003	0.3842 ± 0.003	1.1528 ± 0.009	1.2700 ± 0.078
Ti (%)	0.6678 ±0.0026	0.6174 ± 0.0018	1.8524 ± 0.005	1.5492 ± 0.012
Cr	237.6 ± 17.1	255.2 ± 17.9	315.9 ± 19.0	187.2 ± 16.7
Mn	388 ± 14.4	394.9± 5.0	671.5 ± 18.1	358.5 ± 14.0
Fe(%)	3.8232 ± 0.003	4.0685 ± 0.004	5.9768 ± 0.005	3.5348 ± 0.003
Ni	88.3 ± 6.4	80.5 ± 6.7	59 ± 8.0	54.2 ± 6.5
Cu	129.7 ± 4.7	126.9 ± 4.8	61.8 ± 4.1	117.2 ± 4.6
Zn	223.9 ± 5.1	237.7 ± 5.5	176.3 ± 4.9	228.9 ± 5.3
Ga	119.5 ± 4.7	118.6 ± 4.7	29.7 ± 4.0	124.1 ± 4.6
Ge	27.4 ± 3.6	21.1± 3.9	-------	25.1 ± 3.6
As	57 ± 4.4	52.7± 4.6	-------	44.4 ± 4.7
Rb	113.7 ± 6.5	131.7 ± 6.8	101.1 ± 7.3	102.9 ± 6.9
Sr	232.3 ± 9.5	226.9 ± 9.5	147.2 ± 8.1	238.6 ± 9.3
Y	71.2 ± 8.3	74.3 ± 9.0	66.1 ± 8.1	51 ± 8.5
Zr	419.4 ± 17.2	406.9 ± 17.5	393.8 ± 15.8	394.8 ± 17.4
Nb	72.3 ± 10.2	57 ± 10.1	-------	59.1 ± 9.6
Pb	30.9 ± 2.9	36.1 ± 2.9	16 ± 2.7	28.4 ± 3.0

Table: 5.4 Trace element concentrations (obtained from spectra recorded with absorber only) in the fly ash samples from Panki thermal power station, Kanpur.

Sample ID ⇒	PN 1	PN 2
Elements	Conc	Conc
Ca (%)	0.7264 ± 0.063	0.7568 ±0.062
Ti (%)	1.3461 ±0.012	1.1169 ± 0.011
Cr	226.2 ± .0149	303.3 ± 15.8
Mn	249.2 ± 12.0	256.6 ± 12.3
Fe (%)	2.4497 ± 0.004	2.3044 ± 0.004
Ni	80 ± 5.4	152.5 ± 5.8
Cu	81.7 ± 3.9	57.7 ± 4.1
Zn	83.8 ± 3.7	72.1 ± 3.6
Ga	44.1 ± 3.3	28.7 ± 3.2
As	21.5 ± 3.2	19.6 ± 2.9
Rb	76.8 ± 5.7	68.7 ± 5.4
Sr	193 ± 8.3	147.8 ± 8.4
Y	63.7 ± 7.8	49.8 ± 7.3
Zr	280.8 ± 14.6	250.8 ± 15.5
Pb	13.7 ± 2.0	9.7 ± 1.9

Average concentration of elemental composition of fly ash from the three power plants is compared in Table 5.5, alongwith the literature values [1]. It can be seen from this table that the measured concentrations fall within the ranges of reported values, in general.

It may be concluded that results of PIXE analysis in general agree with the literature values within experimental errors. The technique can be used efficiently to generate data for the trace elements from different Indian coal fly ash for use in the evaluation of their environmental impact and various applications. Further these concentration values may be helpful in developing the pollution abatement approach for various applications of fly ash, a source of major and micronutrient elements for healthy plant growth [2].

It may however be noted that in the fly ash samples from three thermal power stations, there is a high concentration of Mn present, which is generally not found in the fly ash sample taken from other part of the country. Similarly Ga, Ge, Y., Zr, and Nb are also present in considerable amount in these fly ash samples.

In the next stage of our programme it is proposed to carry out PIXE analysis of fly ash samples collected from the air. This analysis will be useful with the human health point of view. Attempt will be made to correlate the toxic elements concentrations with typical diseases occurring in nearby places.

Table 5.5 Average elemental composition of fly ash from the plants under consideration

Elements	HTPS Aligarh	NTPC, Dadri	PANKI, Kanpur	Literature ranges
K (%)	0.7655±.018	0.71 ±0 .005	--------	0.15-3.5
Ca (%)	0.73±.045	0.79 ± 0.03	0.74 ± 0.06	0.11-22.2
Ti (%)	1.17± 0.008	1.17 ± 0.005	1.23 ± 0.01	0.1-2.6
Cr	183±16	248.9 ± 17.6	264.7 ± 15.3	10-1000
Mn	389.9±13.7	453.2 ± 15.3	252.9 ± 12.1	------
Fe (%)	3.5± 0.004	4.35 ± 0.004	2.37 ±0.004	1.0-29
Ni	52.5±6.2	70.5 ± 6.9	116.2 ± 5.6	6-4300
Cu	77.5±4.1	108.9 ± 4.5	69.7 ± 4.0	14-2800
Zn	97.7±4.14	216.7 ± 5.2	77.9 ± 3.6	10-3500
Ga	58.9±3.7	97.9 ± 4.5	36.4 ± 3.2	------
Ge	13.2±4.2	24.5 ± 3.7	-------	------
As	24.8±3.8	51.3 ± 4.5	20.5 ± 3.05	2.3 – 6300
Rb	94.6±6.5	112.3 ± 6.8	72.7 ± 5.55	36-300
Sr	172.5±8.76	186.2 ± 9.1	170.4 ± 8.3	60-3900
Y	48.4±8.06	65.6 ± 8.4	56.7 ± 7.5	------
Zr	366.5±16.7	403.7 ± 116.9	265.8 ± 15.05	------
Nb	134.9±9.1	62.8 ± 9.9	11.7 ± 1.9	------
Pb	13.9±2.2	27.4 ± 2.8	-------	3 – 5000

References

1. S. Sadasivan and B.S. Negi, Sci, Total Environment. **Vol. 103** (1991) 151.
2. M. Dutta and M. Sudarshan, Proceedings of International Conference on International Pollution and control Technology (ICIPACT- 2001, 7,8 10, Dec. JNTU). Hyderabad.