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Environmental Monitoring of Trace Elements in Neem tree Leaves (*Azadirachta indica*) by PIXE Method

Ch. Anjaneyulu¹, S. Lakshminarayana (Retd.)²

^{1,2} Department of Physics, Bapatla Engineering College, Bapatla, India 2. Department of Nuclear Physics, Andhra University, Visakhapatnam, India

Abstract: *Neem tree leaves (*Azadirachta indica*) were collected and analyzed for trace elemental concentrations by Particle-Induced X-Ray Emission (PIXE). An advantage of the PIXE analysis is that about 26 elements can be determined simultaneously. For the PIXE analysis, powder samples were mixed with binder pure graphite powder and thoroughly ground, homogenized and pressed into pellets of 10mm diameter. These pellets were irradiated by the proton beam for respective X-ray intensities. These PIXE experiments were carried out at the Institute of Physics, Bhubaneswar using 3MV pelletron accelerator facility. Good agreement was found between the concentrations of the elements determined and some regional activities.*

Keywords: *Trace elements, PIXE, Neem Tree Leaves, Environmental Pollution.*

I. INTRODUCTION

Trees and other plants make their own food from carbon dioxide (CO₂) in atmosphere, water, sunlight, and a small amount of trace elements in the soil. In the process, they release oxygen (O₂) for us to breathe. Trees remove gaseous pollutants by absorbing them through the pores in the leaf surface. Particulates are trapped and filtered by leaves, stems and twigs and washed to the ground by rainfall. Trees accumulate metals from the soil and act as bio-indicator so far or soil pollution by toxic metals [1]. The elements like Fe, Cu, Mn, Zn, Rb, and Sr are important in metabolic processes in trees. Micronutrients are essential to produce healthy plants. But when plants accumulate excessive levels, a disease called Micronutrient Toxicity Syndrome (MTS) can occur (Maiti et al 2005). Micronutrient Toxicity Syndrome is the accumulation of excessive levels of trace elements (primarily iron and manganese) overtime. The accumulation and distribution of zinc, cadmium, lead and other heavy metals within the plants growing over mineral deposits have been comprehensively studied by many workers [2-5]. Accumulation and absorption of different trace elements by different parts of plant depends on the soil pH value. Trace elements and soil nutrients are readily available when soil pH is at 6.5. When pH rises above this value, nutrient elements such as phosphorus, iron, manganese, copper and zinc will become less available [6]. When soil pH drops below 6.5, manganese can reach a toxic level for some sensitive plants. It is possible to estimate the overall effect of large number of pollutants as total pollution by measuring changes in the plants [7]. This has led to the search for 'bio-indicators' of environmental pollution. In the present study, neem tree (*Azadirachta indica*) has been taken as a reference to study the variation of trace element accumulation in trees at different locations of Visakhapatnam city. In this paper, we used the common species of tree, namely neem tree (*Azadirachta indica*) to bio monitor the concentration of some trace elements like K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, As, Hg, and Pb in different industrial and residential areas of Visakhapatnam city of Andhra Pradesh state in India. The main reason behind this selection is being the fact that neem tree is a conventional tree abundantly appeared everywhere not only in the city but also in entire Andhra Pradesh state in India. PIXE is a versatile nuclear technique like NAA (Neutron Activation Analysis), which is widely used to estimate trace elemental concentration in several environmental samples [8-9], food [10] and biomedical samples [11].

II. SAMPLE PREPARATION

Visakhapatnam is situated at latitude 17°N 42' and longitude 83°E 20'. The main city area stretches north to south on a ridge of 61m high and is like a spoon shaped basin surrounded by hills on three sides with a narrow front eastern zone protruding into the sea (Bay of Bengal). The western side with a group of small hills on the fringe of tidal swamp joins the plains of the city which is surrounded by the Adivivaram hill range, Rushikonda-Kailasagiri hill ranges about 500m high on the North, the Y and Ad hills range (Dolphin hill range about 450m high) on the South. The tidal swamp in the plains is formed by fresh water of Meghadrigadda River and other

streams from Simhachalam. From the meteorological data, 7 months in a year from March to September, the wind direction in Visakhapatnam is predominantly from S-SW-W range where as during the months of November, December and January, a shift in wind direction occurs and it follows SE-E-NE. The months of February and October act as transition period between these two major climatic divisions. Topologically, Visakhapatnam is a low-lying area. This causes air particles to settle down rather than going up there by forcing the dust particles to come close to the ground. Visakhapatnam is a city with several refineries, petrochemical factories, and chemical plants. There is a steel plant and a big thermal power plant (Simhadri) is located not far from the city. It is a fast growing industrial city on the east coast of the south Indian peninsula. The neem (*Azadirachta Indica*) tree samples (leaves) were collected from 10 different locations in and around the industrial areas of Visakhapatnam, namely “Mudasaralova, Yandada, MVP Colony, Scindia, HPCL, Coromandal Fertilizers, Mulagada, Gajuwaka, BHPV and NADKotha Road”. The tree leave samples were collected in February 2006. In the laboratory, leaves were picked from branches and separated into piles of damaged and undamaged. The damaged piles were removed. Each sample was oven dried at 60°C. Leaves were then lyophilized to constant weight and ground to a homogeneous powder using a porcelain mortar and pestle in preparation for PIXE. These powder samples were then mixed with a binder pure graphite powder and boric acid in the ratio of 5:3:1 by weights, in order to avoid the charge buildup during the PIXE experiments [12]. The mixed samples were thoroughly ground, homogenized and pressed into pellets of 10mm diameter. While pelletizing, both faces of the compression die were covered with thin disks of PTFE (Polytetrafluoro ethylene) to avoid direct contact between the powdered sample material and faces of the die. This ensured that the risk of contamination during the sample preparation procedure was kept to a minimum.

III. EXPERIMENT ALPROCEDURE

The present experiments were carried out at Institute of Physics, Bhubaneswar using 3 MV pelletron accelerator facilities. The targets thus prepared were excited with a 2 MeV proton beam and the respective X-ray spectra were recorded with a high resolution Si(Li) detector which was kept at an angle of 90° to the beam direction. The resolution of the detector is 160eV at 5.9keV energy. The targets were kept at an angle of 45° to the beam direction. The X-ray spectra of different samples thus obtained are shown in Figures 1 to 10.

IV. DATA ANALYSIS

In the present study, the PIXE spectra are analyzed using GUPIX95 software program [13-14]. GUPIX is a versatile software package for fitting PIXE spectra for thin, thick, intermediate and layered specimens. This package provides a nonlinear least squares fitting of the spectrum, together with subsequent conversion of the fitted X-ray peak intensities into elemental concentrations using a standardization technique involving fundamental parameters and pre-determined instrumental constants [11]. In GUPIX software package, there is a provision to correct for the overlap of the K_βX-ray component of low Z element with the K X-ray component of high Z element. Another advantage of this package is that no internal standard is required to get concentrations of different elements. Using this software package, the concentrations are to be estimated by employing some fundamental parameters such as total charge collected during irradiation of the sample, energy of the proton beam etc. The concentrations of different trace elements of various samples were incorporated in Table 1.

Table: 1 Comparison of trace element concentrations (µg/g±S.D) in Neem tree leave samples collected from different sites in Visakhapatnam

Element	Mudasaralova (N1) (µg/g)	Yandada (N2) (µg/g)	Scindia (N3) (µg/g)	Coromandal (N4) (µg/g)	M.V.P Colony (N5) (µg/g)	H.P.C.L Area (N6) (µg/g)	Mulagada (N7) (µg/g)	Gajuwaka (N8) (µg/g)	B.H.P.V Area (N9) (µg/g)	N.A.D Area (N10) (µg/g)
K	6744±22.9	5967±11.	1318±4.6	6483±9.7	3938±14.5	1645±12.6	4837±19.3	1932±13.3	2785±13.3	2279±12.9
Ca	18896±54.7	6452±40.	1856±12.	2168±41.2	12304±33.	10881±23.	13963±46.	11529±25.	10935±28.	11127±24.
Ti	846.1±6.5	87.9±2.8	38.9±1.6	105.1±3.1	134.7±3.5	126.0±3.7	146.0±5.0	110.9±3.7	106.6±3.5	105.0±3.3
V	4.8±5.5	7.3±2.1	2±1.1	8.5±2.2	16.5±2.7	8.9±2.6	8.6±3.6	10.5±2.6	9.8±2.6	10.4±2.3

Cr	7.6±2.9	ND	2.2±0.7	9.8±1.5	2.3±2	8.5±1.8	2.8±2.5	5.8±1.8	1.6±1.8	0.8±1.7
Mn	30.0±3.0	18.4±1.6	5±0.7	15.7±1.6	21.2±2.1	51.5±1.9	26.8±2.8	17.8±1.8	24.8±1.9	14.8±1.7
Fe	1235±5.9	214.1±2.	241±1.87	935.2±4.3	612.7±3.4	732.9±4.2	1343±6.7	430.4±3.1	492.6±3.3	464.5±2.9
Co	1.2±6.3	4.6±2.5	0.9±1.38	4.6±3.9	3.0±4.1	0	2.8±6.3	0	0.7±3.4	0
Cu	4.8±1.6	2.7±0.7	ND	5.8±0.7	7.5±1.1	7.4±1	9.7±1.4	7.6±1.0	3.6±1.0	6.6±0.8
Zn	24.7±1.6	3.3±0.7	8.4±0.52	46±1.3	12.5±1.1	30.5±1.3	132.9±2.7	10.4±1.0	22.6±1.1	12.5±0.9
Ga	2.0±1.8	ND	0.3±0.3	ND	3.1±1.2	0.2±1.1	3.8±1.8	0	2.2±1.0	0
As	ND	ND	0.3±0.3	1.2±0.9	1.6±1.1	0.8±1.2	0	0	2±1.1.0	0
Hg	21±6.9	8.4±2.4	2.7±1.3	2±3.5	3.2±4.9	0.4±4.8	6.7±6.9	8.5±3.5	2.2±4.3	2.3±3.6
Pb	13.8±5.5	1.2±1.8	ND	12.9±2.8	3.0±3.6	18.2±3.5	31.3±5.2	9.1±2.8	5.3±3.4	4.8±2.7

N.D: Not Detected; S.D: Standard Deviation

V. RESULTS AND DISCUSSION

The Yandada village is surrounded by agricultural land and has low population and traffic densities. The elemental concentration in the neem tree sample of this area is taken as a standard or control sample (Sampleno.N2). The concentration of potassium is relatively high in Mudasarlova area than Yandada sample. It is very low in Sc India. Higher K concentration in the leaves is a consequence of high transpiration (Lose Water Vapor) rates and the lack of are-translocation system [15]. Potassium (K) levels are important in the production of good quality fruits as well as increasing disease resistance. The concentration of calcium is very high in Mudasarlova sample and low in Sc india sample. Ca is an important part of all plants. It is used in cell walls, and play samajorrolein root and shoot development as well as improving quality and colour of fruits and vegetables (Poffleyet al 2005). Titanium concentration is very high in Mudasarlova sample and very low in Sc india. Vanadium concentration is found to be high in Mudasarlova but very low in Sc india sample compared to the normal one. Chromium concentration is found to be high in Coromandal area but not detected in Yandada sample. The concentration of Manganese is found to be high in the sample of HPCL but very low in Sc india sample. The concentration of Iron is very high in the sample of Mulagada but very low in Yandada sample. A. Doberman and T. Fairhurst determined the optimal range and critical level for occurrence of Fe toxicity in plants as 100-150µg/g & greater than 300-500µg/g respectively [16]. The plant species have the capability to accumulate Fe in greater concentrations than those prescribed the normal range [17]. According to Kabata-Pendias and Pendias, the ratio of Fe: Mn in vegetal tissues and plants should be between 1.5 and 2.5 since, as both are involved in metabolic processes, they must be present in suitable proportions for adequate plant growth [18]. In the present study, the ratio of Fe: Mn in neem leaf samples was much higher than 2.5, thus the imbalance was due to relative excess of Fe at all sites.

The concentration of cobalt is found to be high in the sample of Yandada but not observed in HPCL and NAD samples. The concentration of copper is found to be high in the sample of Mulagada area but very low in normal sample. Kabata-Pendias and Pendias considered Cu concentration of 20µg/g to be the upper limit for toxicity for all the plant samples. In the present study the concentrations of Cu are lesser than this toxic limit. The concentration of zinc is found to be high in the sample of Mulagada but very low in Yandada sample. The Zn concentrations in the plant samples were within the range 27-150µg/g considered to be normal by Kabata-Pendias and Pendias [19]. In the present study the concentration of Zn is within this range and hence can be considered to be normal. The concentration of mercury is found to be high in the sample of Mudasarlova and very low in HPCL sample. The concentration of lead is found to be high in the sample of Mulagada but very low in Yandada sample. The higher concentration of Pb in Mulagada area can be attributed to the automotive exhaust, oil import and export and other industrial sources. Moreover lead released to the air from leaded as oil in stack gas from smelters and power plants will settle on the tree leaves and ultimately get absorbed by them.

VI. ACKNOWLEDGMENTS

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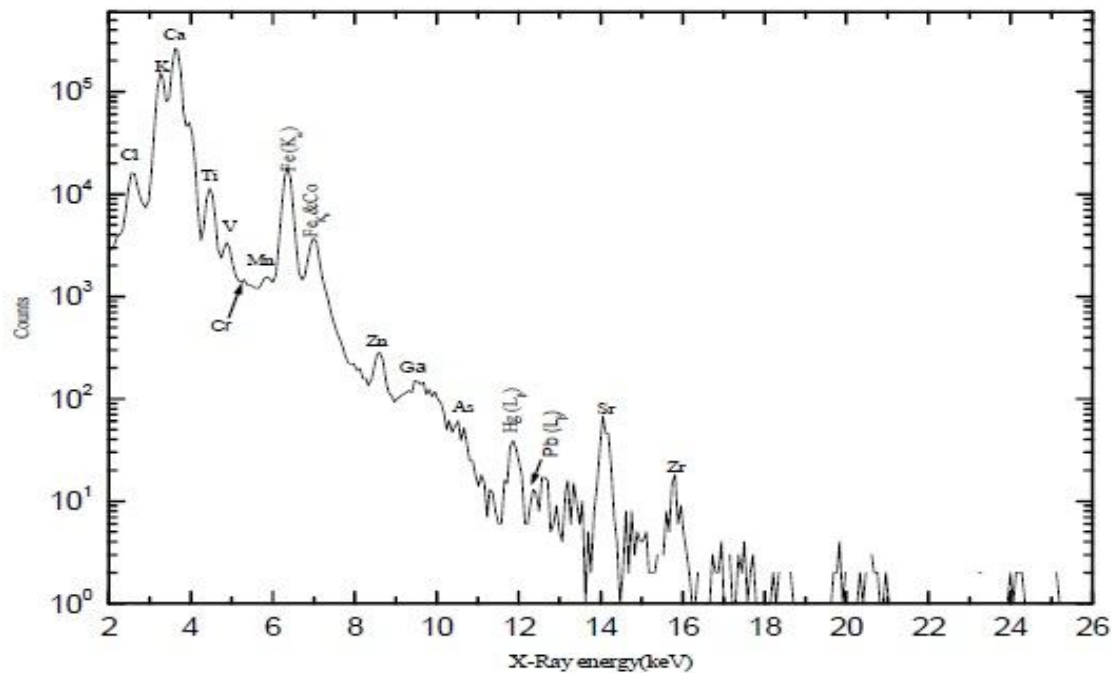


Fig.1 PIXE Spectrum of Neem Leaves sample collected at Mudasaralova area.

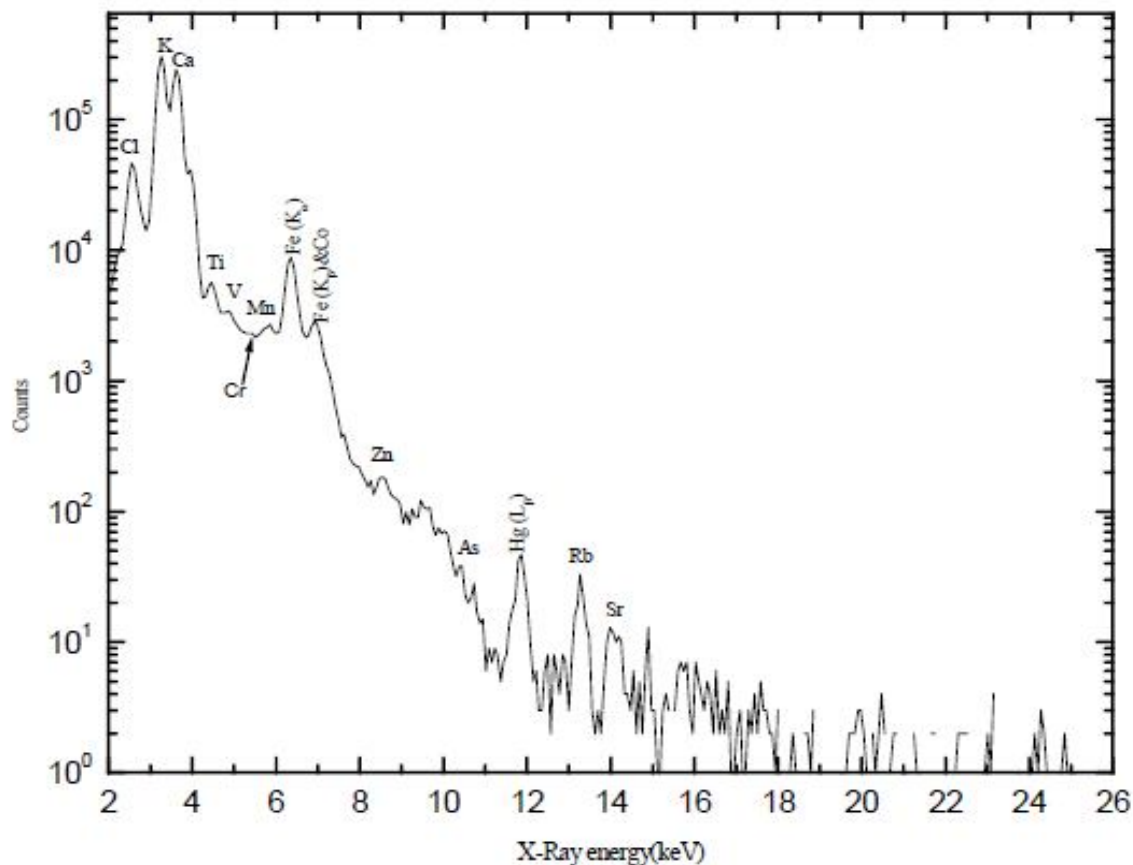


Fig.2 PIXE Spectrum of Neem Leaves sample collected at Yandada area.

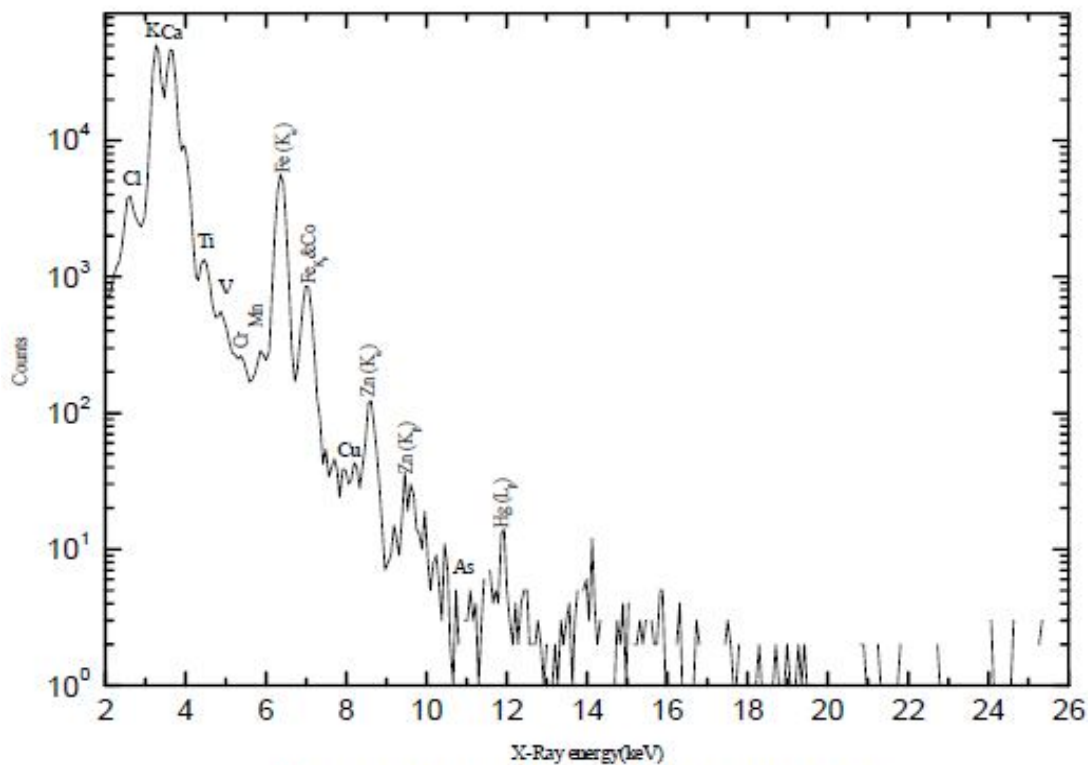


Fig.3 PIXE Spectrum of Neem Leaves sample collected at Scindia area.

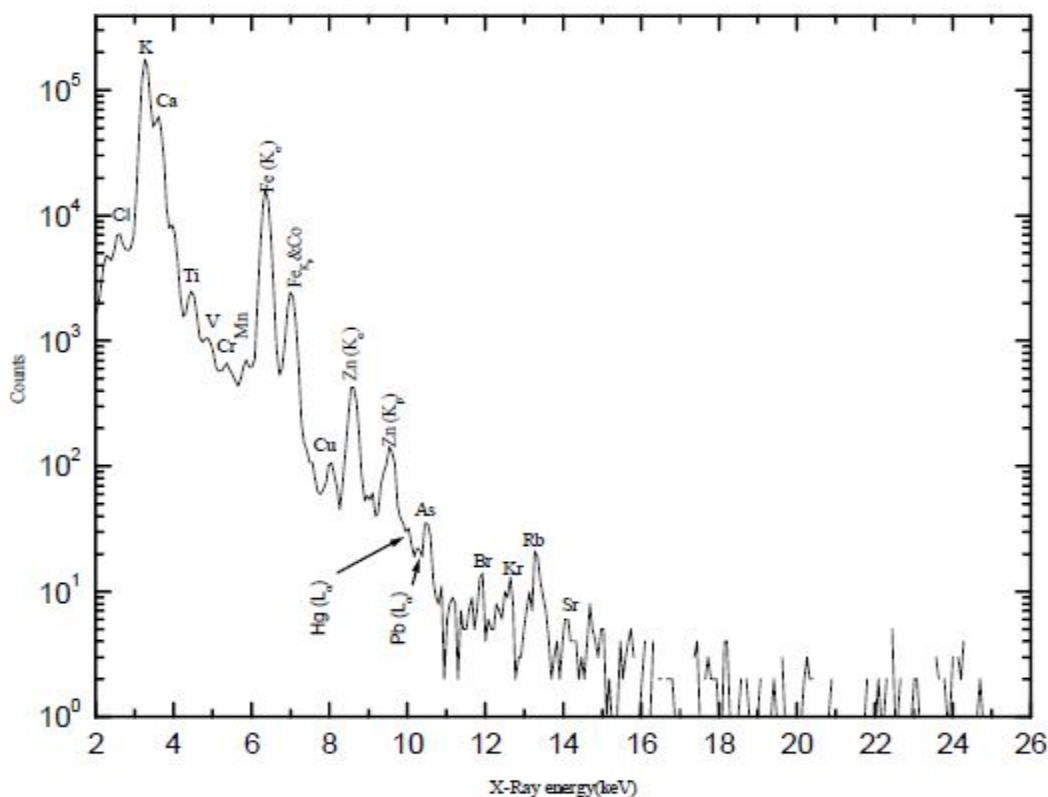


Fig.4 PIXE Spectrum of Neem Leaves sample collected at Coromandal area.

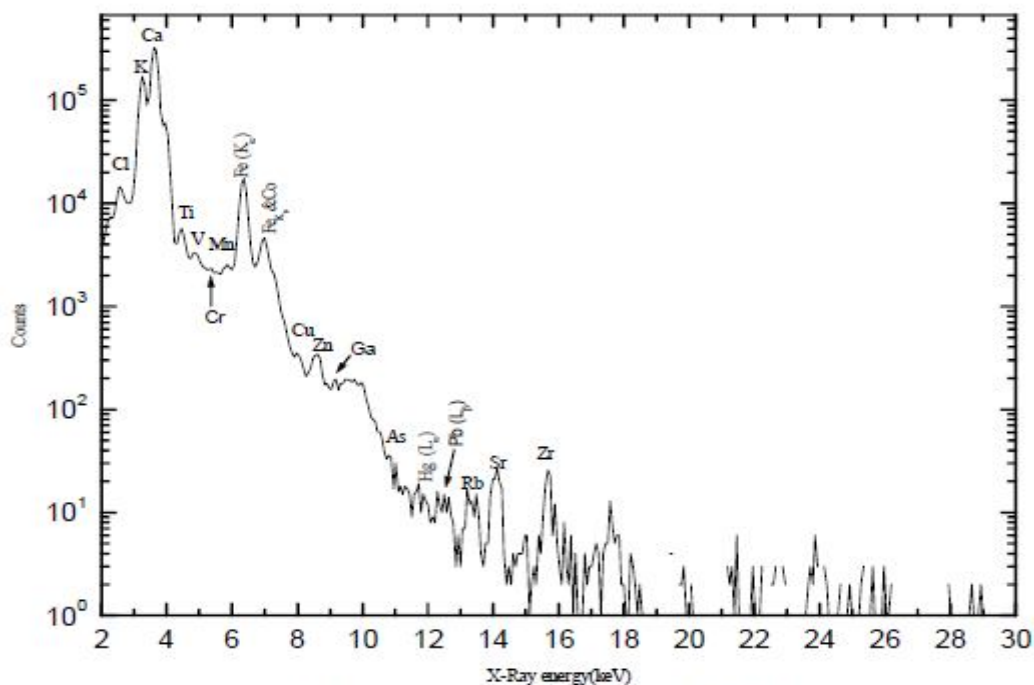


Fig.5 PIXE Spectrum of Neem Leaves sample collected at M.V.P area.

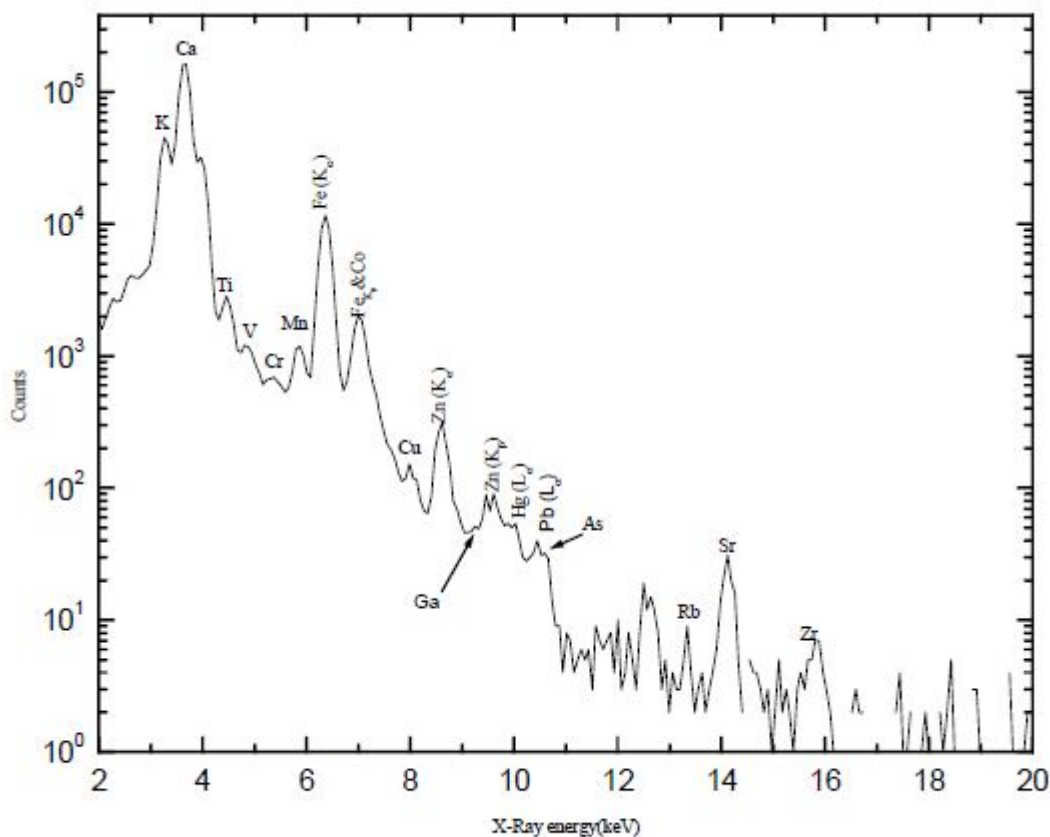


Fig.6 PIXE Spectrum of Neem Leaves sample collected at H.P.C.L area.

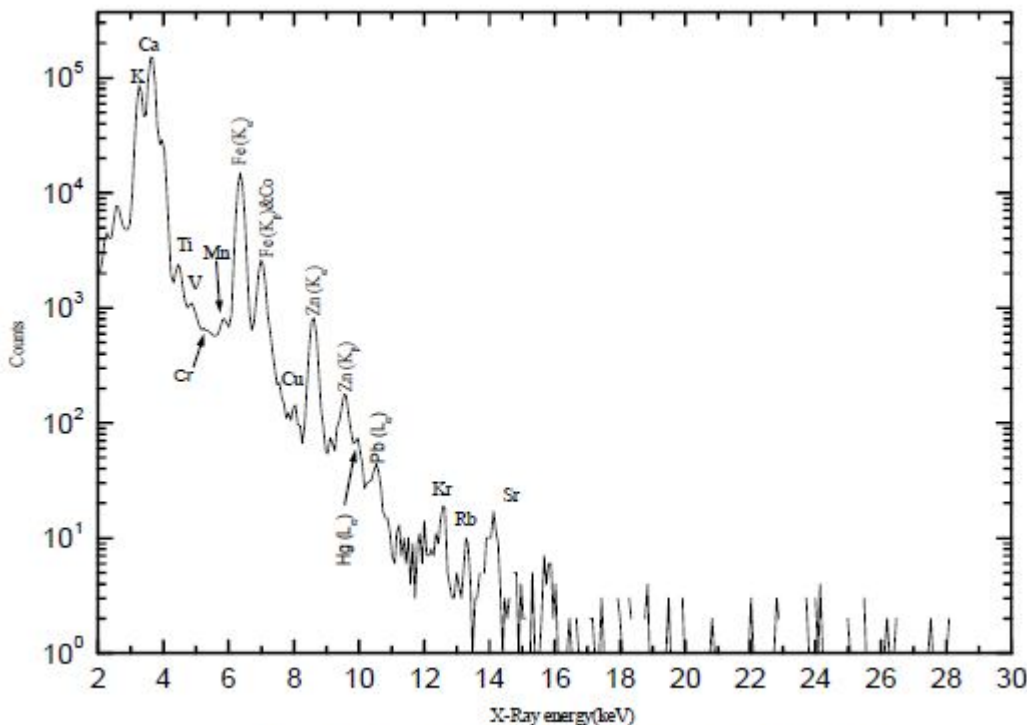


Fig.7 PIXE Spectrum of Neem Leaves sample collected at Mulagada area.

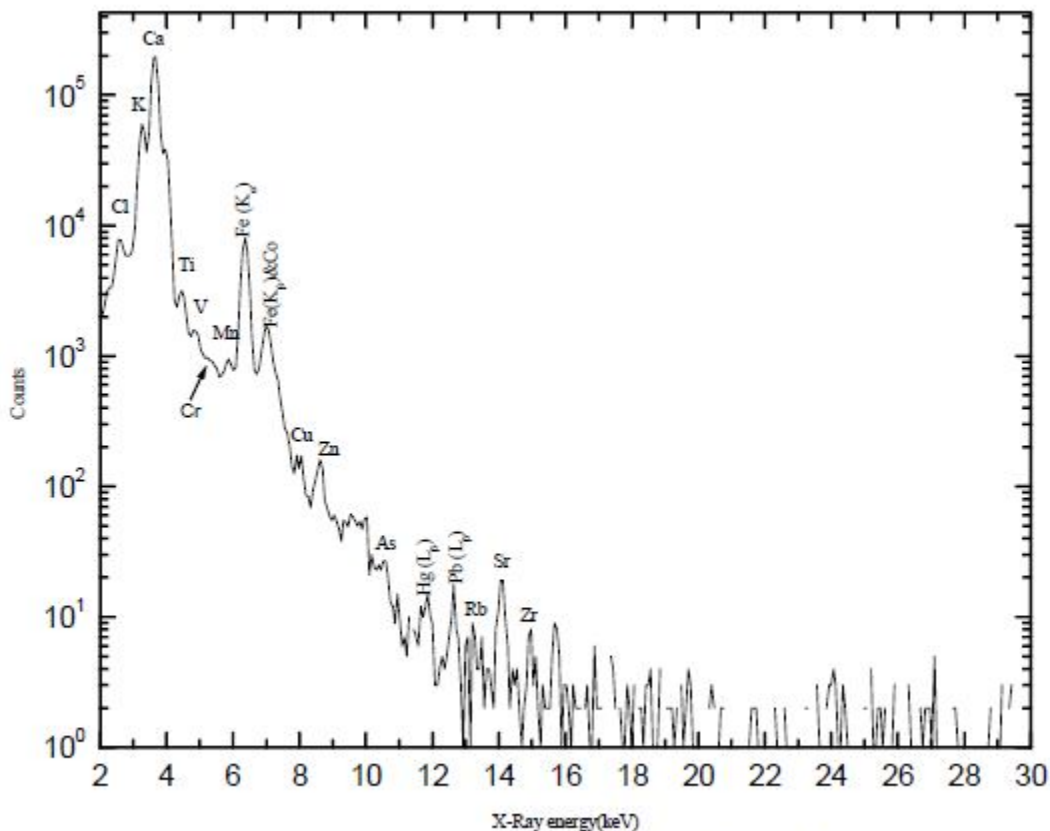


Fig.8 PIXE Spectrum of Neem Leaves sample collected at Gajuwaka area.

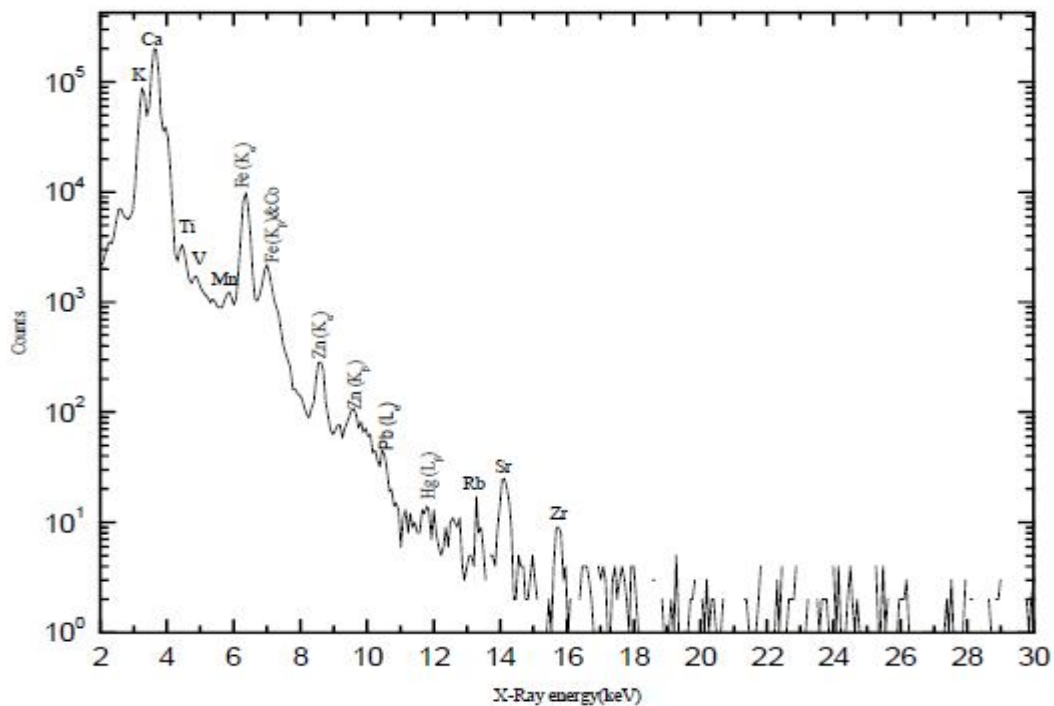


Fig.9 PIXE Spectrum of Neem Leaves sample collected at B.H.P.V area.

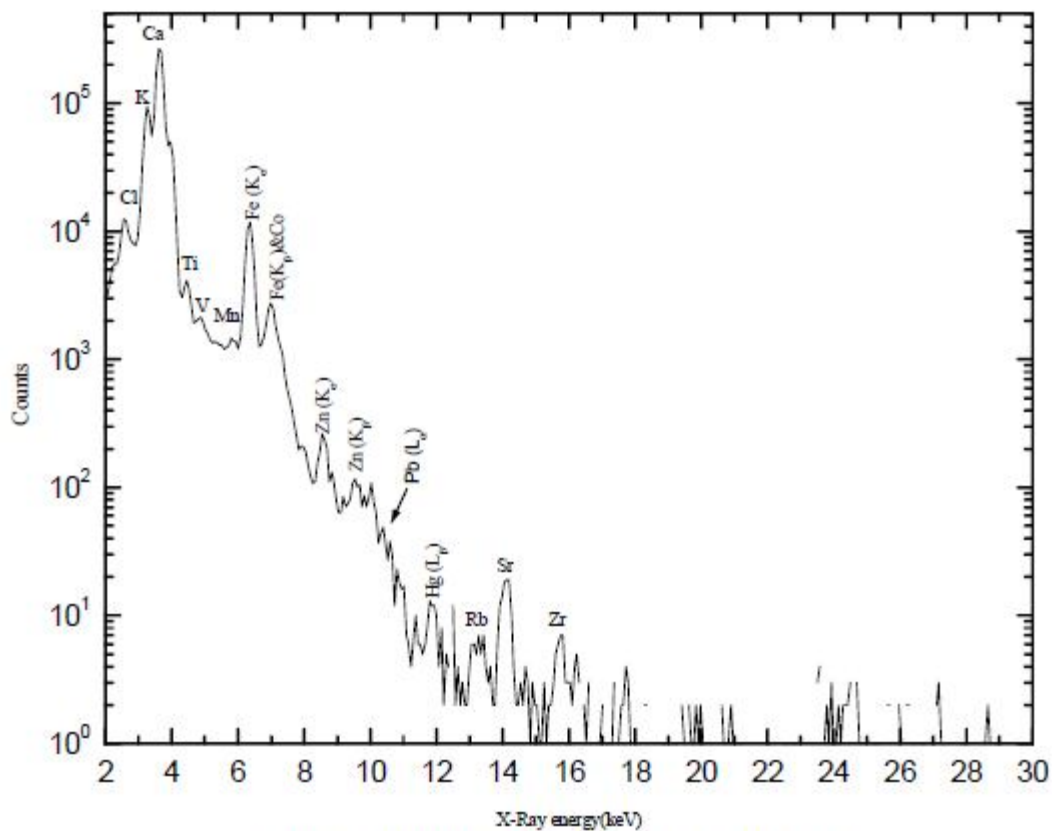


Fig.10 PIXE Spectrum of Neem Leaves sample collected at N.A.D area.

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