

# REACTOR NEUTRON ACTIVATION FOR MULTIELEMENTAL ANALYSIS

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## Abstract

Neutron Activation Analysis using single comparator ( $K_0$  NAA method) has been used for obtaining multielemental profiles in a variety of matrices related to environment. Gold was used as the comparator. Neutron flux was characterised by determining  $f$ , the epithermal to thermal neutron flux ratio and  $\alpha$ , the deviation from ideal shape of the neutron spectrum. The  $f$  and  $\alpha$  were determined in different irradiation positions in APSARA reactor, PCF position in CIRUS reactor and tray rod position in Dhruva reactor using both cadmium cut off and multi isotope detector methods. High resolution gamma ray spectrometry was used for radioactive assay of the activation products. This technique is being used for multielement analysis in a variety of matrices like lake sediments, sea nodules and crusts, minerals, leaves, cereals, pulses, water and soil. Elemental profiles of the sediments corresponding to different depths from Nainital lake were determined and used to understand the history of natural absorption/desorption pattern of the previous 160 years. Ferromanganese crusts from different locations of Indian Ocean were analysed with a view to studying the distribution of some trace elements along with Fe and Mn. Variation of Mn/Fe ratio was used to identify the nature of the crusts as hydrogenous or hydrothermal. Fe-rich and Fe-depleted nodules from Indian Ocean were analysed to understand the REE patterns and it is proposed that REE-Th associated minerals could be the potential Th contributors to the sea water and thus reached ferromanganese nodules. Dolomites (unaltered and altered), two types of serpentines and intrusive rock dolerite from the asbestos mines of Cuddapah basin were analysed for major, minor and trace elements. The elemental concentrations are used for distinguishing and characterising these minerals. From our investigations, it was concluded that both dolomite and dolerite contribute elements in the serpentinisation process. Chemical neutron activation analysis is applied to determine the concentration of REEs in quartzites and other minerals from the Cuddapah basin to understand the REE patterns and mineralogical processes. A comprehensive programme of analysing air, water and soil samples around the mining area is under progress to obtain the correlations between the environmental load with toxic elements and possible health implications vis-a-vis human beings and plant materials. Elemental concentrations of a few varieties of cereals, pulses and leaves were measured. The obtained values were utilised to examine the role of major and minor elements in terms of dietary and curative value of these leaves, cereals and pulses. Trace elements in the leaves could be determined more reliably using radiochemical neutron activation by separating the bulk elements like Na, K and Br, with enhanced sensitivity. A programme to determine nutrient elements and their availability for the plants through soil and water, and nature of species present is initiated. In each set of the experiments, the precision and accuracy were evaluated by determining the concentration of the elements in standard materials. In the studies of minerals USGS standard reference materials AGV-1 and W-1, for nodules and crusts NOD-A-1, for sediments SOIL-7 and for leaves SRM-1571 were analysed along with the samples of interest. CNAA and RNAA were applied for trace element analysis of the SOIL-7 and SRM-1571.

## 1. INTRODUCTION

Environment concerns with water, air, land and their interrelationship viz. human being, fauna and flora. Natural environmental changes may be invisible in a short span of time, but are likely to appear over long periods of time. Rapid industrialisation, deforestation and use of fertilizers, pesticides etc. in modern agriculture, in addition to the urbanisation and vehicular emissions have resulted in serious environmental changes. This reflects in the imbalance of elemental concentrations. The impact of imbalance of elemental concentrations could be understood in the context of health aspects by looking into trace/ toxic element content in our environment. The effect of toxic elements on the environment depends not only on the total concentration but also on their physico chemical state in which they exist. The overall problem of environmental protection is intrinsically linked to man's understanding and interaction with natural biospheric processes. This needs information on the factors that affect

the stability of the biological systems and various ways the anthropogenic loads interact with in these systems. To understand this environmental problem, the natural systems like land, water and air are to be studied. In view of this, it is essential to determine the concentration of elements present in varied matrices like water, food, plant materials, minerals, soil, sediments, particulate matter and air and if possible the chemical states of these elements.

The elements are mainly grouped [1] based on their influence on the environment as (i) As, Be, Cl, Mn, Pb, Sb, Se, Tl and V which characterise the overall ecological situation, (ii) indicator elements that often introduce matter into ecologically important materials: Al, Ba, Fe, Zr, REEs and (iii) toxic elements: As, Cd, Cr, Hg, Ni, Pb and others. Since these elements are present in trace to major concentrations in different environmentally important materials, there is a need for multi-element analysis. Due to relative simplicity, inherent selectivity and sensitivity, Instrumental Neutron Activation Analysis (INAA) occupies an important position among the various analytical methods [2]. Advent of high resolution HPGe based gamma ray spectrometers and on line computer analysis techniques enhanced the simultaneous multielement analysis capability in many cases with or without radiochemical separations [2]. Single comparator NAA known as  $K_0$  NAA [3-5] is now an established semi-absolute method with multielemental analytical capability. It has several advantages as compared to the more frequently used comparative method.

In the present paper, principle of  $K_0$  NAA method, determination of  $\alpha$  and  $f$ , results on the elemental concentrations of standard reference materials, and analysis of sediments, nodules, minerals, plants, leaves, cereals and soil are described. Additionally application of Chemical Neutron Activation Analysis (CNAA) for REE determination in quartzite minerals and Au and Pd determination in matrices containing uranium, copper or iron and Radiochemical Neutron Activation Analysis (RNAA) for the determination of trace elements in leaves are described. Future out look and the thrust areas are also mentioned. Possible application of other nuclear analytical techniques such as RBS, NRA, PIXE, XRF and PGNA are outlined.

## **2. EXPERIMENTAL**

### **2.1 SAMPLING**

#### **2.1.1 Sediments from Nainital lake**

The core samples were collected at different locations in the lake using gravity corer, its inner and outer diameters being 6.0 and 5.2 cm respectively. The length of the core obtained varies from 45 to 51 cm with the help of adjustable piston rod within the silicon packing. Obtained cores were extruded vertically and sliced at 2 cm intervals, were oven dried and homogenised. The textural composition of core samples were mainly clay and slits [6].

#### **2.1.2 Ferromanganese Nodules and Crusts**

The samples from different locations and water depth of the Indian Ocean, collected during the Scandi Surveyor and the 35th Sagar Kanya cruises, were obtained from National Institute of Oceanography, Goa, India. The geographical locations and water depth of these nodule samples are given in ref.[7] and that of crusts are given in ref.[8]. Samples were ground to uniform size and oven dried before using for analysis.

### 2.1.3 Serpentine and Quartzites

The altered and unaltered dolomites, dolerite and two serpentines were collected in the underground asbestos mines making traverses across the formations around Brahmanapalle village of Pullivendla Taluq, Cuddapah district, Andhra Pradesh, India. They were carefully crushed to bring down to the size of 100 mesh (ASTM) sieve. The homogenised materials were subjected to cone and quartering method to prepare the samples for the analysis. The geological set up of these mines are described in ref [9].

### 2.1.4 Leaves, Cereals, and pulses

The leaf samples (L1-L10) were collected in and surrounding areas of Tirupati, Andhra Pradesh, India. On an average 20-50 leaves from the very bottom to top part of the plant were collected giving equal weightage to the tender as well as old leaves. For seeing the effect of soil and environment on the mineral content, Neem leaves were collected both from Tirupati (L10) and Anushaktinagar, Mumbai (L11), India. Leaf samples were washed with deionised water and then with double distilled water. The samples were air dried in a clean drying chamber and dried at 80<sup>0</sup>C over night in an oven. They were crushed to a homogeneous fine powder by pulverisation before sampling. The samples of cereals (C1-C5) and pulses (P1-P7) were collected from different representative places of Tirupati. They were crushed to a homogeneous fine powder by pulverisation and were dried overnight at 105<sup>0</sup> C. Samples are prepared from this powder [10].

### 2.1.5 Gold Standard

A known amount of gold foil (99.999% pure) was dissolved in aqua regia. It was evaporated to dryness and was made up in 0.1M HNO<sub>3</sub>. This solution was used as a standard gold solution.

## 2.2 IRRADIATION

Samples weighing about 25- 50 mg of each were sealed in polypropylene tubes (2mm ID). The sealed tubes containing samples along with gold (5-15 $\mu$ g) were doubly sealed in alkanene, placed in a standard bottle and irradiated in a suitable irradiation position of APSARA reactor, BARC, Trombay, Mumbai. The duration of irradiation was varied from 5 minutes to 7 hours depending on the half life of the nuclide of interest. The neutron flux is around  $\sim 10^{12}$  n.cm<sup>-2</sup>.s<sup>-1</sup>. The sub-cadmium to epi-cadmium flux ratio ( $f$ ) and the deviation from the ideal epithermal neutron flux distribution ( $\alpha$ ) which are important input parameters in K<sub>0</sub> NAA method, were determined experimentally for each position using cadmium ratio method and/or multi isotope detector method [11,12]. The values of  $f$  and  $\alpha$  are given in refs. [11,5]. For the nuclides of short half lives eg., <sup>28</sup>Al, <sup>27</sup>Mg, the cooling period was minimum and it was about a few hours to days for long lived nuclides.

## 2.3 RADIOACTIVE ASSAY

After providing necessary cooling time, polypropylene tubes containing sample and comparator were washed under running tap water, wiped and mounted on a standard perspex plate. Samples were assayed for gamma activity of the activation products using an 80 cc HPGe detector coupled to a PC based 4K channel analyser in an efficiency calibrated position with reproducible sample to detector geometry. The resolution of the detector was 2.1 keV at

1332 keV. Gamma ray standards, e.g.,  $^{152}\text{Eu}$ ,  $^{125}\text{Sb}$ ,  $^{134}\text{Cs}$  and  $^{133}\text{Ba}$  were used for efficiency calibration of the detector in a stable source to detector geometry [13]. Efficiency values were periodically checked using  $^{152}\text{Eu}$  standard sources. The sample to detector distance was maintained between 12 and 15 cm depending upon the level of activity to avoid pile-up and coincidence effects. The activities of radionuclides were followed as a function of time to ensure purity and identity.

## 2.4 CALCULATIONS

Peak areas corresponding to different gamma lines were obtained either by using the SAMPO programme in the case of complex gamma ray spectra or summing the counts under the peak and subtracting the linear Compton background in relatively simple spectra. The peak area was converted to specific count rate ( $A_{sp}$ ) by the equation:

$$A_{sp} = (CL / LT) \cdot [(P_A \cdot \lambda) / (1 - e^{-\lambda t}) \cdot e^{-\lambda T} (1 - e^{-\lambda CL})] \quad (1)$$

where,  $t$  = time of irradiation,  $T$  = cooling time,  $CL$  = clock time,  $LT$  = live time,  $\lambda$  = decay constant of the radionuclide of interest,  $P_A$  = peak area and  $w$  = weight of the element in micrograms (mg).

The concentration of the  $i$ th element ( $C_i$ ) in ppm was calculated using the relation,

$$C_i \text{ (ppm)} = [ A_{p, i} / (A_{sp}^* \cdot K_{anal}) ] \quad (2)$$

where,  $A_{p, i}$  = the specific count rate of the  $i$ th nuclide normalised per gram of the sample,  $A_{sp}^*$  = the specific count rate of the  $^{198}\text{Au}$  per mg of the comparator and the symbol \* refers to the parameters of the comparator.  $K_{anal}$  is the specific count rate ratio of the individual element in the sample to comparator and is calculated using the following equation:

$$K_{anal} = K_{0,exp} [(f + Q_0(\alpha)) / (f + Q_0^*(\alpha))] \varepsilon / \varepsilon^* \quad (3)$$

where,  $\varepsilon$  = the detection efficiency of the detector for the gamma ray energy used,  $f$  = the sub-cadmium to epi-cadmium neutron flux ratio,  $\alpha$  = the deviation from the ideal epithermal neutron flux distribution and  $Q_0(\alpha)$  = the ratio of cross sections and is equal to  $I_0(\alpha) / \sigma_{th}$ , where,  $I_0(\alpha)$  = infinitely dilute resonance integral corrected for the non-ideal epithermal neutron flux distribution and  $\sigma_{th}$  = the thermal neutron cross section. Equation (3) is the simplified form of  $K_{anal}$  as the contribution due to neutron self shielding is negligible. The self shielding correction factor for thermal ( $G_{th}$ ) and epithermal ( $G_e$ ) are approximately equal to 1, as the sample sizes chosen for irradiation were small Relevant nuclear data were taken from the compilations of Browne and Firestone [14] and from the IAEA compilations [15].

## 2.5 RESULTS AND DISCUSSIONS

### 2.5.1 $K_0$ values

$K_0$  is a ratio of four constants of corresponding to the element of interest and the comparator and is given by eqn.(4)

$$K_0 = (\theta \sigma_{th} M^* \gamma) / (\theta^* \sigma_{th}^* M \gamma^*) \quad (4)$$

where  $\theta$  is the isotopic abundance,  $\sigma_{th}$  is the thermal neutron cross section,  $M$  is the atomic mass of the element and  $\gamma$  is the emission probability of the gamma line used. We have measured  $K_0$  factors for fifteen isotopes and obtained a good agreement between the calculated and measured  $K_0$  values. A library of  $K_0$  values for 111 isotopes spanning from fluorine to uranium was made by using the latest nuclear data [14,15] and are given in ref. [11]. The accuracy and consistency of the nuclear data play a significant role in the standardisation of reactor neutron activation analysis. Out of these nuclear constants, data on cross sections and gamma ray emission probabilities are sometimes reported with large uncertainties. Therefore, the accuracy and consistency with respect to the above mentioned constants should be judged individually, consistency being the prime concern.

### 2.5.2 Determination of $f$ and $\alpha$

Sub-cadmium to epi-cadmium neutron flux ratio ( $f$ ) was determined for all the irradiation positions of APSARA reactor using cadmium cut off method where as for PCF at Cirus and tray rod position at Dhruva reactor this ratio was determined by multi isotope method. Another important parameter  $\alpha$ , the extent of deviation from ideal shape of neutron spectrum for each irradiation position was determined using multi isotope/element method. Details of measurements and calculations are given elsewhere [11].

### 2.5.3 Analysis of Standard Reference Materials

Since there is a large variation in the nature of the samples and the concentration of the elements present, it is essential to validate this analytical technique. In this context, a variety of the standard reference materials were analysed. Some of the SRMs analysed by this technique are USGS standard reference materials AGV-1 and W-1, NOD-A-1, SOIL-7 and SRM-1571. A good agreement between the measured values and the reported data was obtained. Percentage deviation of the measured and certified values are plotted in Fig. 1. The over all accuracy is between 2 to 10%. In our studies, as a control of the method of analysis, an appropriate standard was analysed along with the samples in each set of experiments.

### 2.5.4 Sediments from Nainital lakes

The knowledge of sedimentation rates and the elemental concentration levels in sediments from lakes and other water bodies might provide clues to unfold the chronology of the input of pollutants to the water bodies. Eight sets of sediments corresponding to depths from 6 to 51cm were analysed. The IAEA lake sediment standard SL-3 was analysed as a control of the method. Using the experimentally determined sedimentation rate of 0.32 cm/y [6], sedimentation age was calculated for these eight samples and was found to be in the range of 19 to 160 years. The data from different sections of the sediment core are given in Table 1 and represent the history of natural absorption/desorption pattern of the previous 160 years. The elemental concentration of As, Cr, Br, Zn and Cs are found to be more or less constant from bottom to top which could be taken as an indication that there is no anthropogenic pollution of trace elements to Lake Nainital. Samples from different locations of Lake Nainital were analysed and the data show similar trend of elemental concentrations as a function of the depth. A positive correlation of Fe-REE-Th is observed. Thorium is thought to be coprecipitated with REEs as  $\text{Th}(\text{OH})_4$  from water bodies and is absorbed in Fe phases The

condrite normalised REE [16] Ce shows negative anomaly and Eu shows moderate and negative anomaly indicating a reduced atmosphere in the bottom sediments.

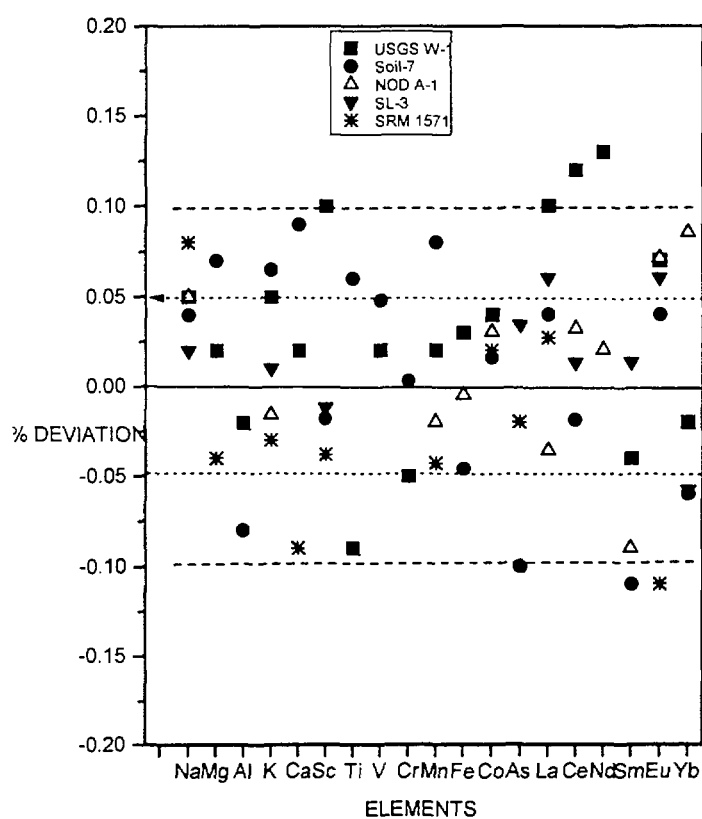


Fig. 1. Comparison of measured and certified elemental concentrations of some standard reference materials.

### 2.5.5 Ferromanganese encrustations from Indian Ocean

Ferromanganese oxide encrustations are common depositional features on exposed rock outcrops in the deep sea. They are mostly found on mid-oceanic ridges, seamounts and raised areas of sea floors of world oceans and significantly differ in their composition and mineralogy [17]. Multielemental analysis together with a varying Mn/Fe ratio is relevant in understanding their distribution in Mn and Fe phases. Three ferromanganese crusts from different locations of the Indian Ocean and another crust from the Lau basin of the Pacific Ocean were analysed by  $K_0$  NAA method for studying the influence of different oceanic conditions on the trace element distributions in ferromanganese crusts. The precision and accuracy of the method were confirmed by measuring the elemental concentrations in a USGS nodule standard NOD A-1. The measured concentrations of elements ferromanganese oxide encrustations (C1, C2, C3 and C4) are given in Table 2. Cobalt was found to be highly enriched in the Afanasiy Nikitin seamount crust. The hydrothermal oxide deposit from Mid Indian Ocean Ridge (MIOR) exhibits a negative Ce anomaly and is associated with a low concentration of trace elements, whereas hydrogenous crusts are enriched in most elements and exhibit a positive Ce anomaly. The crust from north Rodriguez Triple Junction of the MIOR was characterised as of mixed hydrothermal and hydrogenous type, while the crusts from the Afanasiy Nikitin seamount and a topographically elevated region exhibit hydrogenous properties. The rare earth elements were found to be highly enriched in the crust of the Afanasiy Nikitin seamount and elevated region compared to the crust from MIOR. The thorium content was remarkably high for hydrogenous crusts. A Co-Sb correlation was observed particularly in seamount crust.

TABLE 1. Elemental concentrations of Sediment samples (in ppm unless % is indicated). N. D. = not detected

Element	S1	S2	S3	S4	S5	S6	S7	S8
Depth(cm)	51	45	39	33	27	19	12	6
Na%	0.54± 0.01	0.42± 0.02	0.48± 0.02	0.40± 0.02	0.49± 0.02	0.44± 0.03	0.46± 0.03	0.42± 0.02
K%	3.22± 0.15	2.28± 0.12	2.45± 0.18	2.42± 0.02	2.74± 0.06	2.44± 0.02	2.39± 0.12	2.30± 0.11
Sc	14.60± 0.45	12.07± 0.55	12.70± 0.81	11.32± 0.62	14.85± 0.72	13.83± 0.71	12.38± 0.52	12.13± 0.90
Cr	113.82 ±4.50	90.58± 3.60	91.90± 4.20	91.60± 5.07	96.00± 4.17	103.49 ±5.02	104.23 ±4.11	85.83± 3.12
Mn%	0.172± 0.01	0.128± 0.01	0.126± 0.01	0.117± 0.01	0.142± 0.01	0.119± 0.01	0.129± 0.01	0.136± 0.01
Fe%	5.23± 0.18	4.18± 0.27	4.01± 0.21	4.14± 0.09	5.00± 0.09	4.22± 0.13	4.11± 0.24	3.88± 0.07
Co	32.27± 1.81	20.60± 1.01	21.65± 1.20	20.00± 0.54	22.28± 1.12	20.45± 0.42	21.76± 0.90	23.86± 1.01
Zn	N. D.	75.23± 4.03	110.90 ±5.10	105.32 ±4.31	126.93 ±4.17	97.38± 5.72	111.45 ±6.32	66.07± 2.72
Ga	8.96± 0.52	13.52± 0.82	N. D.	18.64± 1.01	N. D.	9.39± 0.73	10.52± 0.85	9.84± 0.72
As	20.39± 0.85	19.91± 1.31	13.50± 0.80	10.77± 0.25	17.46± 1.07	17.10 ±1.10	16.51± 1.05	18.17± 1.24
Br	0.85±0 2	N. D.	1.13± 0.06	1.00± 03	1.40± 0.06	1.38± 0.06	1.30± 0.10	1.85± 0.11
Rb	115.38 ±6.50	100.23 ±5.40	128.20 ±7.10	N. D.	136.64 ±5.39	110.69 ±4.13	N. D.	100.74 ±3.52
Sr	N. D.	496.10 ±22.00	350.20 ±15.21	190.00 ±14.21	232.10 ±16.20	332.05 ±17.00	375.10 ±20.10	532.00 ±10.23
Cs	21.34± 1.52	12.44± 0.82	14.28± 0.83	14.14± 0.94	14.73± 0.62	11.05± 0.52	14.05± 0.43	13.85± 0.61
Ba	645.23 ±15.20	881.00 ±30.10	794.00 ±18.00	798.00 ±45.12	752.10 ±32.00	780.00 ±25.10	821.00 ±30.10	838.00 ±35.50
La	42.16± 2.44	29.31± 1.14	31.40± 1.30	32.04± 2.10	37.06± 1.96	33.17± 2.01	33.13± 1.48	32.55± 2.03
Ce	50.32± 3.21	33.98± 2.10	44.15± 2.70	42.04± 2.11	47.42± 1.43	43.70± 2.13	35.00± 2.21	41.60± 2.70
Nd	25.97± 1.51	14.97± 1.05	20.21± 1.14	17.91± 1.15	N. D.	19.64± 1.18	18.47± 1.23	11.56± 1.12
Sm	6.19± 0.18	5.03± 0.32	5.63± 0.41	5.71± 0.12	7.26± 0.22	5.86± 0.14	6.46± 0.71	5.61± 0.26
Eu	1.09± 0.08	1.12± 0.08	1.00± 0.07	0.97± 0.06	1.15± 0.04	0.89± 0.05	0.96± 0.04	0.96± 0.07
Dy	3.79± 0.20	1.76± 0.12	3.65± 0.17	3.30± 0.18	4.10± 0.21	3.70± 0.18	4.30± 0.24	4.21± 0.23
Yb	4.12± 0.21	6.45± 0.41	2.63± 0.14	3.28± 0.15	3.87± 0.25	2.58± 0.16	2.21± 0.13	2.24± 0.12
Lu	0.61± 0.04	0.96± 0.04	0.95± 0.05	1.08± 0.06	0.89± 0.05	1.04± 0.06	N. D.	0.72± 0.05
Hf	N. D.	1.83± 0.07	1.97± 0.10	2.88± 0.11	2.35± 0.07	2.46± 0.14	2.51± 0.08	2.85± 0.17
Th	12.31± 1.01	13.04± 1.10	11.27± 0.91	13.81± 1.00	11.28± 0.85	13.57± 1.02	11.48± 1.03	13.88± 1.12

TABLE 2. Elemental Concentrations of ferromanganese Oxide Encrustations (in mg.kg<sup>-1</sup> unless % is indicated).

Element	C1	C2	C3	C4
Na%	1.12 ± 0.07	0.80±0.04	2.79 ± 0.13	1.51±0.09
K	5798 ± 246	3814±151	2316 ± 117	1280±76
Sc	9.83 ± 0.41	10.76±0.38	7.11 ± 0.28	16.69±0.78
Cr	N. D.	51.70±	70.6 ± 6.4	N. D.
Mn%	16.5 ± 0.9	21.2±1.4	12.1 ± 0.7	N. D.
Fe%	19.2 ± 0.9	16.9 ± 0.7	21.9 ± 0.8	37.2±1.4
Co	12300 ± 396	2331±98	879 ± 39	74±5
As	121 ± 9	163.5±12	247 ± 14	449±22
Sb	80.4 ± 3.1	16.2±0.7	12.2 ± 0.6	8.73±0.4
Cs	301±26	851±64	136 ± 9	83±9
Hf	N. D.	4.64±0.34	7.67 ± 0.53	N. D.
W	101.4 ± 6.5	82.7±3.6	12.2 ± 0.5	N. D.
Th	81.2 ± 5.4	114.2±8.3	3.7 ± 0.2	N. D.
La	239.4 ± 11.2	286.0 ± 12.2	201.4 ± 8.2	14.7±0.9
Ce	2037 ± 106	1530±78	169 ± 9	11.12±0.6
Nd	184.3 ± 9.7	222.5±13.2	125.3 ± 7.1	N. D.
Sm	37.6 ± 2.2	48.5±2.5	38.2 ± 2.3	N. D.
Eu	8.21 ± 0.48	12.20±0.68	11.32 ± 0.63	N. D.
Tb	3.2 ± 0.33	3.83±0.33	2.62 ± 0.33	N. D.
Ho	2.78 ± 0.34	3.46±0.39	N. D.	N. D.
Yb	16.85 ± 0.89	21.85±1.13	13.94 ± 0.83	1.51±0.08
Lu	2.68 ± 0.14	3.43±0.22	2.24 ± 0.09	N. D.
Ce*	+0.61	+0.407	-0.37	-
Mn/Fe	0.86	1.25	0.55	-

N. D. - not detected, Ce\* = Cerium anomaly calculated as  $\log[3Ce/(2La+Nd)]$  as given in ref.[16]

## 2.5.6 Ferromanganese Nodules from Indian Ocean

The ferromanganese nodules are mostly found at the interface of Ocean waters and the underlying sediment on the ocean bed and are associated with minor and trace constituents of alkali, alkaline earth metals, transition metals, REEs and other heavy elements. Characterisation of nodules might provide information on physical, chemical and biological activities taking place in the ocean. A total of five ferromanganese nodules from different locations and water depth of Indian Ocean were analysed along with SRM NOD P1. The measured concentrations of various elements in the nodule samples are presented in Table 3. A few elements, namely, Sc, Sb, Hf, W and Th have been estimated for the first time in the Indian Ocean nodules.

The Fe enriched hydrogenous nodules were associated with higher concentration of most of the minor and trace elements. Slow growth rate, high retention time and favourable depositional environment are attributed to their enrichment. Hydrogenous nodules characterised by low Mn/Fe ratio, found at shallow region of the Indian Ocean, indicates lower mobility of Fe component compared to the Mn in the oceanic environment, leading to the precipitation of Fe as its oxyhydroxide. Cobalt was found to have strong affinity towards Fe. Tungsten and thorium are found positively correlated with iron and are reasonably enriched in the hydrogenous nodules compared to the diagenic one. Rare earth elements are probably incorporated on iron oxyhydroxide phase by adsorption processes. The REE abundance increases with the increase in the Fe content and is in good agreement to the earlier



reports on the nodules of Pacific Ocean. It has been shown that the rare earth elements (REEs) are adsorbed but not co-precipitated with the iron oxyhydroxide phase.

TABLE 3. Elemental Concentrations of ferromanganese nodules of Indian Ocean (in ppm unless % is indicated).

Elements	N1	N2	N3	N4	N5
Na %	2.44±0.21	2.56±0.23	1.75±0.18	2.08±0.14	2.32±0.13
K %	0.57±0.04	0.58±0.04	0.40±0.03	0.50±0.04	0.48±0.04
Mn %	15.3±0.6	19.1±0.9	18.6±0.8	16.9±0.7	17.2±0.4
Fe %	16.5±0.7	21.2±0.8	13.9±0.7	11.3±0.4	5.5±0.3
Sc	15.65±0.32	22.92±0.81	13.72±0.36	15.33±0.78	10.92±0.42
Co	3220±163	5362±214	2180±96	2174±106	1128±49
As	76±8	110±9	77±6	61±5	39±4
Sb	18.9±0.7	21.6±0.8	19.5±0.8	17.9±0.6	12.2±0.6
Cs	321±7	379±16	216±12	267±9	718±24
Hf	6.52±0.37	6.61±0.35	8.54±0.46	7.14±0.49	3.40±0.22
W	67.1±4.3	77.8±6.8	49.2±3.9	46.6±4.5	42.5±4.4
Th	42.5±2.4	50.5±3.3	48.5±2.9	47.2±2.9	24.6±1.4
La	142.2±6.4	257.5±10.2	204.8±7.9	184.4±8.6	98.6±8.2
Ce	951±34	1862±83	1246±48	948±39	502±23
Nd	137.4±7.2	196.6±9.8	167.7±7.6	138.4±9.7	88.3±7.2
Sm	28.2±1.1	42.8±2.1	42.1±2.1	34.4±1.1	20.3±0.9
Eu	6.74±0.56	11.14±0.66	8.70±0.83	7.55±0.72	4.76±0.38
Tb	3.24±0.33	4.82±0.34	3.31±0.37	3.09±0.29	2.62±0.33
Ho	4.78±0.64	6.89±0.91	6.53±0.87	5.78±0.64	2.97±0.32
Yb	19.32±0.59	32.43±1.08	24.22±1.03	21.41±0.98	9.85±0.63
Lu	3.48±0.13	6.22±0.24	4.62±0.13	3.82±0.13	1.58±0.11
Ce*	+0.24	+0.21	+0.18	+0.16	+0.24
Mn/Fe	0.93	0.90	1.34	1.50	3.11
(La/Lu)*	0.76	0.81	0.82	0.88	0.98
ΣREE	1296.36	2420.40	1707.98	1346.85	730.98
Ce/La	6.68	7.24	6.08	5.14	5.09

Ce\* = Cerium anomaly, calculated using the relation  $\text{Log}[3\text{Ce}/(2\text{La}+\text{Nd})]$ , as given in ref.[16]  $(\text{La/Lu})^* = (\text{La}_{\text{sample}} / \text{La}_{\text{NASC}}) / (\text{Lu}_{\text{sample}} / \text{Lu}_{\text{NASC}})$

### 2.5.7 Dolomites, Dolerite and Serpentine

Serpentines are a class of secondary minerals derived by alteration in magnesium rich silicate minerals. It is reported that serpentine and associated asbestos are formed due to hydrothermal solutions accompanying the dolerite intrusives into dolomite host rock. The black and green serpentines are potential sources of asbestos. With an aim to understand the process of serpenisation, investigations on the composition of two types of dolomites (unaltered and altered dolomites) and two types of serpentines along with intrusive rock dolerite obtained in the asbestos mines of Brahmanapalle in Cuddapah basin, Andhra Pradesh, India were carried out. As many as 23 elements are measured. The elemental concentrations for the serpentines as well as the unaltered and altered dolomites and dolerite obtained from four independent determinations are given in Table 4. The major elements present in the five varieties are Mg, Ca, Al and Fe. From the variation of Mg concentration, it is clear that both dolomite and dolerite contribute Mg to serpentines. Absence of Ca in black serpentine could be that it is replaced by Mg in the serpenisation. The REEs decrease in the order: dolerite → black serpentine → yellow serpentine → dolomite. Elements like Ti, V, Cr and a few REEs are absent in unaltered dolomite where as these elements are present in serpentines and

dolerite. From these observations, it is clear that these elements were contributed in the serpentinisation only by dolerite.

TABLE 4. Elemental Concentrations of Intrusive rock (Dolerite), two Serpentine and Dolomites ( in mg.kg<sup>-1</sup> unless % or ng.g<sup>-1</sup> is indicated).

S.N	Element	Dolerite	Black serpentine	Yellow serpentine	Altered dolomite	Unaltered dolomite
1	Na	1325.47±79.51	162.37±7.46	93.28±5.02	86.90±5.87	654.67±18.15
2	Mg%	9.22±1.1	22.72±1.86	18.11±0.58	8.28±0.18	12.91±7.4
3	Al%	1.89±0.11	4.00±0.17	0.11±0.005	0.11±0.005	0.17±0.01
4	Cl	N. D.	400.10±11.20	255.23±2.92	288.67±9.12	132.33±5.21
5	Ca%	8.75±1.15	N. D.	0.55±0.02	18.10±1.32	25.46±1.76
6	Sc	27.13±1.12	25.29±1.07	0.16±0.01	0.50±0.02	0.22±0.01
7	Ti %	0.48±0.03	0.70±0.04	N.D.	N.D.	N.D.
8	V	209.50±14.12	172.42±8.53	N.D.	N.D.	N.D.
9	Cr	N. D.	53.66±3.23	N. D	N. D.	N. D.
10	Mn	2921±160	2722±54	28.69±0.09	144.02±9.45	145.31±3.59
11	Fe%	7.94±0.20	5.00±0.38	0.22±0.01	N.D.	N.D.
12	Co	30.51± 1.85	37.31±2.33	4.36±0.23	5.63±0.31	4.73±0.26
13	As	N.D.	4.99±0.18	13.41±1.16	6.21±0.11	0.76±0.05
14	Ba	N.D.	N.D.	545.00±53	222.02±17.06	158.58±9.23
15	La	13.72±1.05	10.94±0.68	1.82±0.04	3.07±0.06	1.28±0.08
16	Ce	41.32±2.16	24.25±1.51	N.D.	N.D.	8.32±0.67
17	Sm	2.97±0.15	1.77±0.08	0.48±0.03	0.23±0.01	0.22±0.02
18	Eu <sup>#</sup>	990.05±60.10	350.23±20.11	100.16±5.10	50.28±2.12	20.06±1.13
19	Dy	N.D.	9.19±0.57	0.27±0.01	N.D.	N.D.
20	Yb	2.99±0.00	2.22±0.10	N.D.	N.D.	N.D.
21	Au <sup>#</sup>	N.D.	13.20±1.01	N.D.	20.25±1.52	10.12±0.85

N. D. - not detected, '<sup>#</sup>' - ng. g<sup>-1</sup>

### 2.5.8 Edible and Medicinal Leaves, Pulses and Cereals

The role played by micro nutrients and trace elements in the biochemical functions of human life and their impact on human life are important. These are supplied through food chain. Additionally carbohydrates, proteins and minerals are provided through food items like cereals, pulses and leaves. The investigations are aimed at measuring the concentrations of minerals required for human beings viz: major elements like Ca, P, K, Mg, Na, Fe and trace elements like Zn, Co, I, Cu, Mn, Mo, F, Se, Ni, Cr, Cd, Si, V and Sr. Phosphorous could not be measured by gamma spectrometric based NAA. It is also important to know the variation of these elements in these items from different places and environment. A comprehensive programme of determining the elemental profiles in soil, water, seeds and leaves is initiated.

Elemental concentrations of a few varieties of leaves which are used either as a natural ingredient in ayurvedic medicine preparations or as reliable items for human diet and SRM-1571 are determined by K<sub>0</sub> NAA method. The leaves analysed, their local names and scientific names are given in Table 5 Data obtained on one of the varieties studied (Neem), collected from two different places are given in Table 6. These data have been used to see the effect of soil condition on the trace element concentrations in these leaves. Elemental concentrations of a few varieties of cereals and pulses which are used as natural ingredients for human diet are determined. The cereals and pulses analysed, their local names and scientific names are given in Table 7. Al, Cl, Mg, Mn, Na, K and Ca were determined using

short irradiation times, where as Br, Zn, Co, Fe, La, Sm, Cr, Rb, Se, Sn and Hg required long irradiation times and the elemental concentrations for 17 elements measured in cereals and pulses, in the present studies are given in Tables 8 and 9. An attempt has been made to analyse the results on the measured concentrations of major and minor elements in terms of the average intake and the dietary value of these leaves, cereals and pulses. The data obtained on the major and minor elemental concentration of the cereals and pulses can be used to evaluate the potentiality of these grains in their use for average intake and the dietary values. A programme is initiated on evaluating the uptake of elements by plants from different soils.

### 2.5.9 Palladium and gold determination by CNAA

Measurement of trace elements in presence of large amounts of Fe, Cu and U by NAA is very difficult due to the spectral interferences and also becomes complicated due to the fission product contribution from the fission of uranium. In such cases, it becomes imperative to preconcentrate elements of interest and decontaminate from the major elements and measure the concentrations by NAA. A reliable Chemical Neutron Activation Analysis (CNAA) method was developed to measure the trace amounts of Au and Pd present in matrices that may contain uranium, copper and iron [18,19]. Pd and Au were preconcentrated on a mini column containing anion exchanger Dowex 1X8 (100-200 mesh ) in Cl<sup>-</sup> form. The column was irradiated and the activities produced were measured using a this window HPGE and a Si(Li) systems. Concentrations were evaluated by comparison method. Standard addition method was used to arrive at the lowest detection limits. Under the ideal interference free conditions, an absolute detection limit of 0.12ng for Pd and 0. 1ng for Au were achieved. This is being used routinely to measure trace amounts of Au and Pd in different matrices.

Table 5 Sample Description of the leaves

Sample Ident.	Local Name	Scientific Name	Medicinal Uses
L1	Kadi patta	Murraya koenigii (L.) spr	Dysentery, Bruised, Snake bite, Eruptions
L2	Chauli(small)	Amaranths polygamus L.	Diarrhoea, Seminal debility, Leucorrhoea and Monorrhagia and Antidote for Snake poison
L3	Kanuga.	Pongamia pinnata (L.) pierre	Flatulence, Dyspersia, Diarrhoea, Cough, Leprosy, Gonorrhoea, Foul ulcers, Sores, Rheumatic pains and Bleeding piles
L4	Drum stick	Moringa oleifera Lam	Dental caries, Swellings, Hydrocele, Headache and Paralysis
L5	Eucalyptus	Eucalyptus globulus Labill	Rheumatism, Burns, Mosquito repellent, Infections of the Upper Respiratorytract, Chronicbronchitis, Asthma, Phthis, Insect and Vermin repellent and Some skin diseases.
L6	Methi	Amaranthus hybridus L.	Gonorrhoea, Eczema, Scorpion-sting, Snake bites, Cough, Dysentery
L7	Ambadi	Hibiscus cannabinus L.	Purgative, Healing
L8	Chauli	Amaranths gangetilus L.	Astringent, Menorrhagia, Diarrhoea, Dysentery, Haemorrhage, Ulcerated conditions of throat and mouth

L9	Pudina	Mentha spicata L.	Fewer, Bronchitis, aphthae and antidote to poison
L10	Neem	Azadirachta indica A. juss	Ulcers, Boils, czema, Smallfox, Blood purification, Skin diseases and as a antiseptic solution

TABLE 6. Elemental concentrations of Orchard Leaf (NIST SRM-1571) and Neem leaves

Element	Units	SRM 1571		Neem Leaf	
		Measured	Reported	Tirupati(L10)	Mumbai(L11)
Na	µg/g	88.7±6.8	82.0±6.0	100.4 ±6.5	541.5±17.7
Mg	%	0.59±0.02	0.62±0.02	0.49 ±0.03	0.76±0.03
Al	µg/g	330.5±7.5	310-410	116.2±7.2	309.3±21.3
Cl	µg/g	650.0±30.0	690	5300±400	8300±500
K	%	1.42±0.09	1.47±0.03	2.84±0.09	1.11±0.06
Ca	%	1.89±0.03	2.09±0.03	3.06±.034	4.02±0.051
Sc	ng/g	86.5±5.1	90.0	-	-
Ti	µg/g	56.9±4.2	-	-	-
V	µg/g	0.52±0.02	-	1.66±0.06	4.26±0.08
Mn	µg/g	87.0±8.2	91.0±4.0	16.97±1.16	36.5±2.1
Zn	µg/g	29.3±4.3	25.0±0.3	-	-
As	µg/g	8.3±0.6	10.0±0.2	-	-
Br	µg/g	8.5±0.7	9.5±1.1	7.07±0.5	3.86±0.24
Sr	µg/g	34.1±1.5	37.0±1.0	115.0±10.1	138.3±4.4
Sb	µg/g	2.6±0.3	2.9±0.3	-	-
I	µg/g	-	-	3.09±0.6	-
Cs	µg/g	-	-	-	1.89±0.13
Ba	µg/g	-	-	74.98±3.41	-
La	µg/g	1.13±0.07	1.1±0.07	0.33±0.005	-
Sm	ng/g	130.0±10.0	114±20	-	-
Eu	ng/g	20.2±2.3	24±3	-	-

"-" not detected

TABLE 7. Sample Description of the cereals (C1-C5) and pulses (P1-P7).

Sample Identification	Local Name	Scientific Name
C1	Wheat	Triticum aestivum L.
C2	Paddy	Oryza sativa L.
C3	Bajra	Pennisetum typhoides (Burm.f) Staff & Hubb.
C4	Ragi	Eleusine Coracana(L.) Gaertn
C5	Jowar	Sorghum vulgare Pers
P1	Methi	Trigonella foenum.graecum L.
P2	Moong	Phaseolus aureus Roxb.
P3	Chanadal	Cicer arietinum L.
P4	Til	Sesamum indicum L.
P5	Chanli	Vigna sinensis (L.) Hassk
P6	Horse Gram	Dolichos biflorus L.
P7	Tur Dal	Cajanus cajan(L.) Mill.

TABLE 8. Elemental Concentrations of Cereals (in mg.kg<sup>-1</sup> unless % is indicated)

Element	C1	C2	C3	C4	C5
Na	42.3± 2.3	195.9± 12.8	84.77± 2.87	114.8± 1.4	106.62± 3.55
Mg%	0.24± 0.025	0.92±0. 032	0.703± 0.014	0.44± 0.034	0.69± 0.019
Al	2.6± 0.43	1801.88 ±47.7	995.27± 98.46	N. D.	886.8± 50.6
Cl%	0.17± 0.004	0.33±0. 033	0.262± 0.006	0.106± 0.002	0.14± 0.006
K%	0.43± 0.011	0.48± 0.095	0.54± 0.051	0.57± 0.28	0.65± 0.263
Ca%	N. D.	0.11± 0.04	N. D.	0.35± 0.023	0.048± 0.003
Mn	40.88± 3.83	151.6± 7.99	32.9± 1.87	267.3± 6.99	19.72± 2.04
Br	2.63± 0.38	2.38± 0.52	0.38± 0.022	0.97± 0.082	1.65± 0.077
Zn	191.81± 14.12	92.60± 5.59	154.22± 10.12	61.79± 2.52	77.62± 4.65
Co	1.33± 0.09	0.51± 0.02	0.96± 0.04	0.37± 0.02	2.71± 0.14
Fe	1915.30 ±98.71	816.75± 54.28	467.11± 11.56	489.57 ±21.12	1376.21± 50.21
La	0.172± 0.032	0.46± 0.053	N. D.	4.8± 0.06	N. D.
Sm	N. D.	0.14± 0.003	N. D.	N. D.	0.16± 0.01
Rb	N. D.	165.94± 10.72	115.12± 8.58	71.59± 4.51	N. D.
Cr	N. D.	55.70± 2.23	N. D.	N. D.	N. D.
As	N. D.	0.144± 0.032	N. D.	N. D.	N. D.

*N. D. Not detected*

TABLE 9. Elemental concentration of Pulses (in mg.kg<sup>-1</sup> unless % is indicated)

Element	P1	P2	P3	P4	P5	P6	P7
Na	391.2± 23.6	27.65± 3.51	167.88 ±12.78	230.68 ±4.16	149.05± 8.5	54.53± 0.92	52.58±5 .8
Mg%	0.87± 0.04	0.88± 0.035	0.87± 0.025	1.15± 0.05	0.79± 0.030	0.51± 0.023	0.34± 0.025
Al	N. D.	N. D.	649.6± 41.29	778.3± 6.93	1079.3± 67.73	586.81± 37.8	185.6±1 0.6
Cl%	0.273± 0.008	0.108± 0.001	0.19± 0.003	0.095± 0.002	0.064± 0.0016	0.07± 0.001	0.04± 0.002
K%	1.62± 0.04	1.32± 0.03	1.24± 0.152	0.93± 0.11	1.91± 0.015	1.55± 0.042	1.6±0.2
Ca%	0.297± 0.013	0.173± 0.015	0.24± 0.014	1.16± 0.018	0.4± 0.086	0.344± 0.035	0.115± 0.017
Mn	20.6± 0.8	15.53± 0.4	31.12± 1.19	22.57± 1.9	43.9± 1.25	48.82± 0.86	10.1± 0.6

Br	0.63± 0.02	0.5± 0.009	13.22± 0.4	5.7± 0.34	2.27± 0.12	2.81± 0.24	5.12± 0.25
Zn	167.12± 12.02	155.29 ±10.05	86.56± 2.13	82.94± 3.16	96.54± 1.84	127.91± 8.12	60.93 ±2.35
Co	3.02± 0.21	2.14± 0.11	0.74± 0.04	1.78± 0.04	0.45± 0.02	0.75± 0.05	0.54± 0.02
Fe	1261.16 ±88.40	855.90 ±25.23	1181.45 ±63.35	934.51 ±29.53	806.04± 25.43	1466.65 ±32.28	912.64± 35.21
La	N. D.	N. D.	0.174± 0.023	14.45± 0.76	0.25± 0.025	0.027± 0.0012	0.74± 0.032
Se	54.38± 3.15	N. D.	30.22± 0.93	28.3± 1.35	8.77± 0.364	N. D.	44.2± 4.85
Sm	0.089± 0.004	N. D.	N. D.	0.033± 0.002	0.084± 0.025	N. D.	N. D.
Rb	203.52± 11.24	83.4± 5.32	77.11± 3.45	125.61 ±7.53	191.67± 11.20	N. D.	51.9± 5.84

### 2.5.10 Rare Earth Elements (REE) in quartzites by CNAA

Trace amounts of uranium are present in the quartzites of Cuddapah basin. estimation of REEs in quartzites by NAA becomes erroneous due to the contribution from the fission of uranium. A preconcentration chemical procedure was developed and tested to estimate REEs in quartzites. This procedure was standardised using radiotracers in the separation of REEs from synthetic mixtures to arrive at the chemical yields and applied to quartzites. Quartzites were brought into solution by digesting with HCl in presence of HF. Boric acid was added to remove the excess fluoride and the solution was brought to 1MHCl .REEs and U were coprecipitated as oxalates by adding calcium chloride. The precipitate was dissolved in 9M HCl and loaded on an anion exchange (Dowex 1X8, Cl<sup>-</sup> form) column to adsorb uranium. The effluent containing REEs was subjected to NAA.

### 2.5.11 Determination of trace elements in leaves by RNAA

In many naturally occurring materials like biological and minerals, Na is a major element .In leafy materials, in addition to sodium, Br and K are present as major constituents. In NAA activation products of these elements make the measurements nearly impossible. In view of this, it is essential either separate these major element prior to activation (CNAA) or after the activation (RNAA). If the matrix does not contain fissionable materials, then it would be better if the chemical separations are carried out after the activation. Trace elements are determined in leaf samples and in SRM-1571 by RNAA with enhanced sensitivity [20]. Irradiated sample was digested in perchloric acid medium to expel radiobromine. Radiosodium and radiopotassium were separated from the solution by passing it over HAP column in 8M HNO<sub>3</sub> for Na removal and 1M HNO<sub>3</sub> for K removal. For the first time elements Ti and V were measured in SRM-1571. These were compared with the results obtained by CNAA on the same standard. A similar programme of measuring the trace elements in blood samples after removing radiosodium is initiated. Preliminary data indicate that trace elements like Cr, Fe and Zn could be measured reliably.

### 3. FUTURE OUTLOOK

#### 3.1 ENVIRONMENTAL MONITORING AROUND CUDDAPAH BASIN

Cuddapah basin is rich in minerals like asbesots, lime stone, barytes and uranium bearing rocks. Mining of these minerals load the environment with particulate matter which is a health concern. A comprehensive programme of monitoring air, soil, water and plants around this area is initiated in collaboration with Department of Mineral Chemistry, S.V.U. P.G. Centre, Cuddapah.

#### 3.2 ENVIRONMENTAL MONITORING AROUND AGRA

Agra is an industrially developing area. A programme of monitoring the soil, water and dew in and around Agra is initiated to evaluate the impact of the pollutants by Dayalbagh Educational Institute, Agra and we are extending the required analytical services.

#### 3.3 NUCLEAR ANALYTICAL TECHNIQUES

Apart from utilising NAA for analysing varied matrices, nuclear analytical techniques using ion beam analysis are being developed with a view to utilise them for material characterisation. We are setting up facility for RBS, NRA and PIXE at the Folded Tandem Ion Accelerator (FOTIA) in B.A.R.C. where low energy ion beams will be made available. The main areas of research and development envisaged are depth profiling of low Z materials in different industrially important materials using NRA, high tech materials using RBS and multi elemental analysis in biologically and environmentally important materials using PIXE. It is also proposed to set up PGNA for analysing low Z materials in environmental samples.

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