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TITLE

Search for heavy metals in specified groups of the Bangladesh population, (part of a coordinated programme on nuclear-based methods for analysis of pollutants in human hair)

FINAL REPORT FOR THE PERIOD

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Title of the Project

Search for heavy metals in specified groups of the Bangladesh Population.

Institute where research is carried out

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Chief Scientific Investigator

Dr. Mozammel Husain.

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Original time period of the contract was 15th Dec., 19[illegible] to 14th Dec., 19[illegible] but due to unavoidable reasons the work took longer time.

Description of the work

The findings of the work are described in the enclosed paper which is intended to be published in a journal.

TRACE ELEMENT CONCENTRATION IN HAIR OF THE BANGLADESHI POPULATION*

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ABSTRACT

The concentration of 12 trace elements has been determined in the head hair of an adult population in Bangladesh. In total 102 samples were analysed using the external beam PIXE method. The absolute concentrations have been determined using a calibration obtained from the NBS standard Orchard Leaf. The results obtained from the present study have been compared with the values recently reported in literature.

* This research was performed under the IAEA-BAEC Contract No. 2136/RB.

INTRODUCTION

The pollution of the biosphere by trace elements, specially by heavy metals is a global concern of the modern time. In a recent study at Bettele (quoted in Ref. 1), it has been indicated that in future the quality of human life would be most affected by the environmental stress due to heavy metal contaminations. At present it is second only to pesticides in this respect.

All pollutions in the living environment ultimately affect the man. So, the study of trace element pollution in man deserves the most urgent attention. It is also important to have a knowledge of the normal levels of trace elements in man so that any deviation from it can be monitored at times. It is to these ends that considerable efforts are being made all over the world to determine trace element contents in different human tissues and body fluids. Of all human tissues, the head hair has been identified to be most suitable[1] for the analysis of many trace elements in man, firstly because it is easily accessible to experimentation for in-vitro analysis. Secondly, during the growth period, hair being exposed to circulating blood, lymph and extracellular fluids, keeps a continuous record of the changes of the trace element concentrations in the body[1,2]. However, if the data on the trace element contents of hair are to be used as an indication of the body burden, the external contamination of hair is to be taken into account. In that case, hair data are to be supplemented by those of tissues and body fluids.

Realizing the importance of trace element analysis of hair and the availability of powerful methods like NAA, AAS, PIXE, etc., IAEA started an internationally coordinated study programme on this subject. The present study is a part of that programme. In this study, all the samples were analyzed by the Proton-induced X-ray Emission (PIXE) method. In all 102 hair samples from an adult population in Bangladesh were analyzed. The results on the contents of 12 elements that were possible to be detected with the PIXE method are reported here.

2. EXPERIMENTAL

Each hair sample (~5 g) was collected from different areas of head with a clean stainless steel clipping scissors. According to the prescribed procedure in ref. 1, the samples were washed twice with acetone, three times with double distilled water and finally once with acetone. The washed samples were air dried for 24 hours in a clean room. A known quantity of each dry sample was charred at 180°C for one hour in a pyrex beaker. This step of charring the sample was necessary to easily powder the material. The charred sample after cooling and weighing was ground to powder with an aluminum carbide mortar and pestle. Before this operation a sample of chromatographic grade cellulose powder (Whatman) was ground in the mortar for blank correction, if any.

From the powdered material of hair, 50 mg pellets, 7 mm diameter and 1 mm thick, were prepared with a graduated stainless steel hand-press pellet maker (Perkin-Elmer). The pellets were mounted in 35 mm slide frames with adhesive tape and preserved in a desiccator until irradiation.

Method of Analysis

In this investigation, the external beam PIXE method was used to determine trace element contents in hair. The details of the method have been described elsewhere[3-5]. A schematic diagram of the experimental setup is given in Fig. 1. Kapton foils of 1.12 mg/cm^2 thickness instead of Be were used as the proton exit windows. Proton beams of nominal energy of 2.5 MeV from the 3 MeV Van de Graaff accelerator at the Atomic Energy Centre, Dacca, were used for the irradiation of the targets. After energy loss in the exit window and the air path, the beam energy on the target was about 2 MeV. The targets were placed at 45° with respect to the beam direction. The beam spot at the exit window was 4 mm. This gave an irradiation spot on the target well within the pellet diameter. The irradiation

current was about 30 nA, which gave reasonable counting rate. The integrated current for each irradiation was 20 μC.

Characteristic X-rays were detected with a 30 mm^2 Si(Li) detector (Ortec). A 44 mg/cm^2 plastic absorber was used to reduce the argon background in air. The pulses after amplification were analyzed with a 4096 channel Canberra Analyzer. The data reduction was done manually. Corrections for the overlapping peaks were made from the K_α/K_β ratio measured separately under identical conditions using cellulose targets doped with the element concerned. A typical X-ray spectrum of a hair sample is illustrated in Fig. 2.

3. RESULTS AND DISCUSSION

Calibration and the Sensitivity of the Method

Trace element concentrations in hair were obtained by comparison with a standard. The NBS Orchard Leaves (SRM 1571) standard was used for this purpose. To obtain the calibration curve shown in Fig. 3, similar pellets of the standard were irradiated in an identical geometry of measurements. The calibration curve is the variation of X-ray yield per ppm per microcoulomb with the atomic number of the element. The certified values of concentrations of the elements were used to construct this yield curve. The concentration of the element in the sample was then simply obtained from

$$ppm_i = \frac{Y_i \; T W}{Q X_i}, \text{ at constant geometry,}$$

where Y_i = X-ray yield of the element in the sample, T = deadtime correction factor, Q = integrated charge (μC), Y_i = calibration factor and W is the dry weight factor for the sample.

It has been mentioned before that the samples were charred at 180°C to make it easy to grind them to fine powder. In doing so, it was believed that at this low temperature of

charring, there would not be any appreciable less of trace elements. The average weight loss due charring was found to be 26±4%. However, individual weight loss was used in the calculation of concentrations. The blank correction was found to be negligible. The sample homogeneity was tested by irradiating several pellets from the same material and it was found within 3%. The geometry variation from sample to sample positioning was negligible.

The applicability of the calibration curve in Fig. 3 for analyzing trace elements in other biological matrices such as hair has been discussed in detail in ref. 5. In view of the X-ray yields obtained in a number of light element matrices widely varying in proportions of the major elements (H, C, N, O, etc.), it was observed that such calibrations are universally valid for all biological matrices. The systematic deviation of the curve for different matrices was estimated to be less than 15%. This can, however, be further reduced, if the concentration of the major elements in a given biological matrix is known.

The minimum detection limits (MDL) of different elements in the hair matrix are given in Table 1. The MDL of an element, from the consideration of statistical errors in counting, was defined as the amount which would yield an X-ray intensity at least equal is 3 σ of the background under the peak taken in an interval equal to the FWHM of the peak. For a 20 μC irradiation, it was about 0.3 ppm in the region of iron.

Distribution of Trace Elements in Hair

In all 102 samples were analyzed. The subjects were randomly chosen from about 500 employees of the Atomic Energy Centre, Dacca. The age distribution of the selected sample group is shown in Fig. 4.

With the present method, under the experimental conditions mentioned before, twelve elements were found to have concentrations above the detection limits in hair. A summary of the results is shown in Table 2. In the calculation of the mean, the data points which do not form a part of the close distribution in the plot of frequency vs logarithm of

concentration were not considered. The arithmatic and the geometric mean for each element was calculated by considering only the data above the background. The procedure described in ref. 1 for data presentation could not be used to obtain mean values, as the distributions obtained were nongaussian because of the small number of samples. The mean values shown here are, therefore, artificially high for those elements where a fraction of the samples were found to have concentration below the background level. Similarly, in the calculation of the median only those data points above the background, which form close distribution in log normal frequency plot, were considered. The frequency distribution of the concentration of different elements is shown in Fig. 5. In these plots, concentration rather than log of concentration is shown as the absissa for easy readability. The data with too high concentrations are not included in this presentation. The mean and the median in Fig. 5 correspond to the close log distribution as discussed earlier.

It can be seen from the comparison in Table 2 that the arithmatic mean of concentrations above the background is in general agreement with the values reported in literature[1], except in the case of Cu. Concentrations of Cu determined in the present work are relatively lower. It is noted that baseline data on Sr in hair is not available in literature. So, no comparison for this element was possible. So far Pb in hair is concerned, very few data are available. One Canadian study (quoted in ref. 1) reported values of Pb for rural population in the range of 0.5 - 25 ppm with a median of 9.1 ppm while for the urban population, it was 0.5 - 35 ppm, the median being 15.3 ppm. These are rather high values compared to those reported here

The peak for Pb L_{α} line (10.55 keV) coincides with the AsK_{α} line. But in the absence of AsK_{β} line at 11.72 keV and from the consideration of the Pb L_{α} / L_{β} ratio, the peak at 10.55 keV was considered to be purely due to Pb L_{α} indicating the absence of As in the hair samples analyzed here. It may be noted that the detection limit for As in

hair under the conditions of the present study is about 0.4 ppm.

4. CONCLUSION

The concentration of twelve elements (K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr and Pb) in human head hair has been determined using the external beam PIXE method, in 102 samples from an adult population in Bangladesh. The mean values of the concentrations obtained in the present work are found to be comparable to those reported in literature, except for Cu, in which case our values are relatively lower.

ACKNOWLEDGEMENT

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Trace Elements in Human Hair Garland Publishing. N.Y., 1977.

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Table 1 - Minimum detection limit (MDL) in Hair matrix for 20 μC irradiation.

Elements	Atomic Number	X-ray peak	MDL (ppm)
K	19	K_{α}	9
Ca	20	K_{α}	3.28
Ti	22	K_{α}	0.90
Cr	24	K_{α}	0.52
Mn	25	K_{α}	0.41
Fe	26	K_{α}	0.31
Ni	28	K_{α}	0.34
Cu	29	K_{α}	0.33
Zn	30	K_{α}	0.40
Br	35	K_{α}	0.44
Sr	38	K_{α}	0.76
Pb	82	L_{α}	0.71

Table - 2 : Trace Element contents in Human Hair in ppm (μg/g) (102 samples)

Elements	No. of samples with concentration above background.	No. of samples with too high concentration.	Arithmatic Mean* (ppm)	Geometric Mean* (ppm)	Median** (ppm)	Range of values in literature (ref. 1) A.M. (ppm)	Range of values in literature (ref. 1) G.M. (ppm)
K	77	8	42.9±22.4	36.9±1.8	38.7±11.6	16.8 - 95	14.2 - 42
Ca	102	4	655 ±256	606 ±1.48	579 ±35	510 - 2650	386 - 3000
Ti	17	-	3.20±1.43	2.91 ±1.55	2.57±0.52	-	2.4 - 3.6
Cr	40	4	2.45±1.43	2.06 ±1.85	2.04±0.32	0.46 - 4.1	0.34 - 2.6
Mn	95	10	2.26±1.37	1.85 ±1.95	1.81±0.26	1.1 - 23	0.49 - 8.8
Fe	102	9	25.9±10.9	23.6 ±1.6	23.3±0.4	60 - 122†	27 - 106
Ni	32	3	1.12±0.65	0.94 ±1.85	1.03±0.17	1.01 - 18	2.8 - 14
Cu	102	1	6.78±1.60	6.60 ±1.25	6.79±0.32	11 - 25.4	9.6 - 20.6
Zn	102	1	141 ±34	137 ±1.25	131 ±1.2	138 - 308	128 - 261
Br	98	2	2.15±0.83	2.00 ±1.48	2.01±0.38	2.3 - 39	1.92 - 27
Sr	49	10	2.47±1.06	2.25 ± 1.56	2.24±0.60	-	-
Pb	98	14	3.86±2.12	3.28 ±1.84	3.39±0.54	-	-

* Uncertainties are the standard deviations.
** Uncertainties are due to counting statistics.
† For some of the studies AM's are not available.

FIGURE CAPTIONS

Fig. 1 A schematic diagram of the PIXE experimental setup.

Fig. 2 An X-ray spectrum from a Hair sample.

Fig. 3 Concentration calibration curve.

Fig. 4 Age distribution of the sample group.

Fig. 5 Trace Element distribution in Hair.

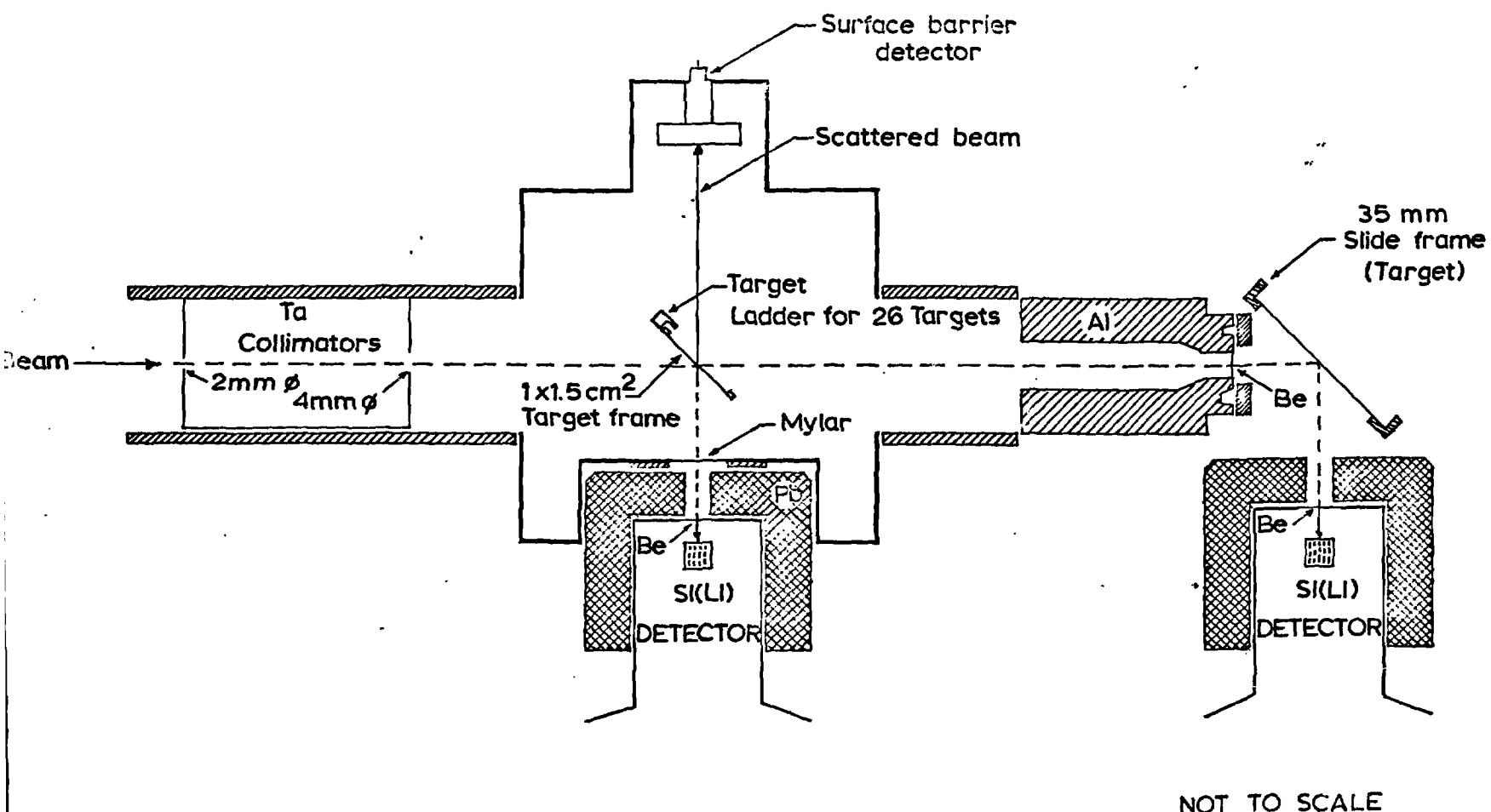
Surface barrier detector
Scattered beam
35 mm Slide frame (Target)
Target Ladder for 26 Targets
Ta Collimators
Beam
2mm ø
4mm ø
1x1.5 cm²
Target frame
Mylar
Al
Be
Be
Si(Li) DETECTOR
Be
Si(Li) DETECTOR
NOT TO SCALE

Fig 1

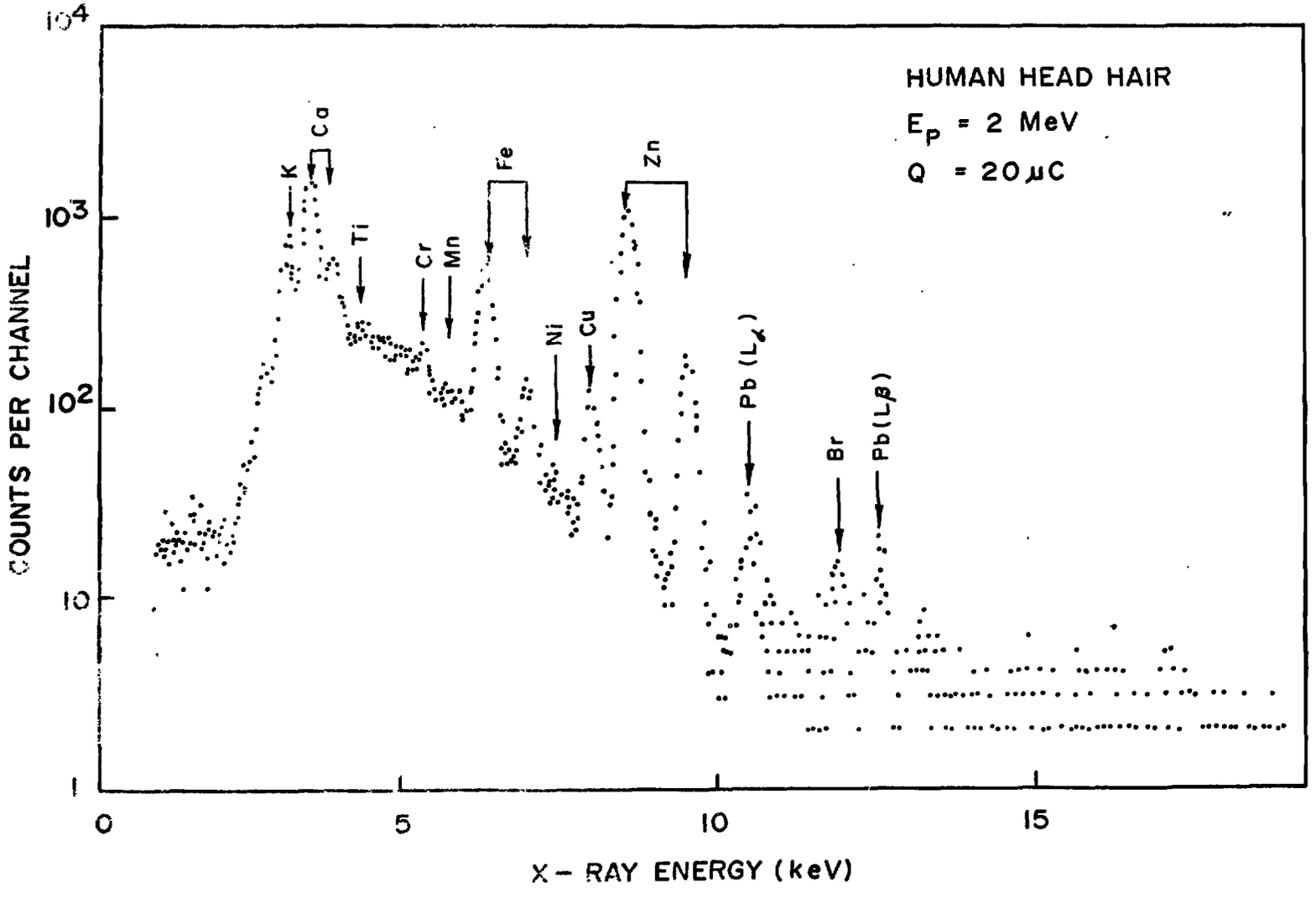
HUMAN HEAD HAIR
E_p = 2 MeV
Q = 20 μC
COUNTS PER CHANNEL
X – RAY ENERGY (keV)
K
Ca
Ti
Cr
Mn
Fe
Ni
Cu
Zn
Pb (L_α)
Br
Pb (L_β)
10^4
10^3
10^2
10
1
0
5
10
15

Fig. 2

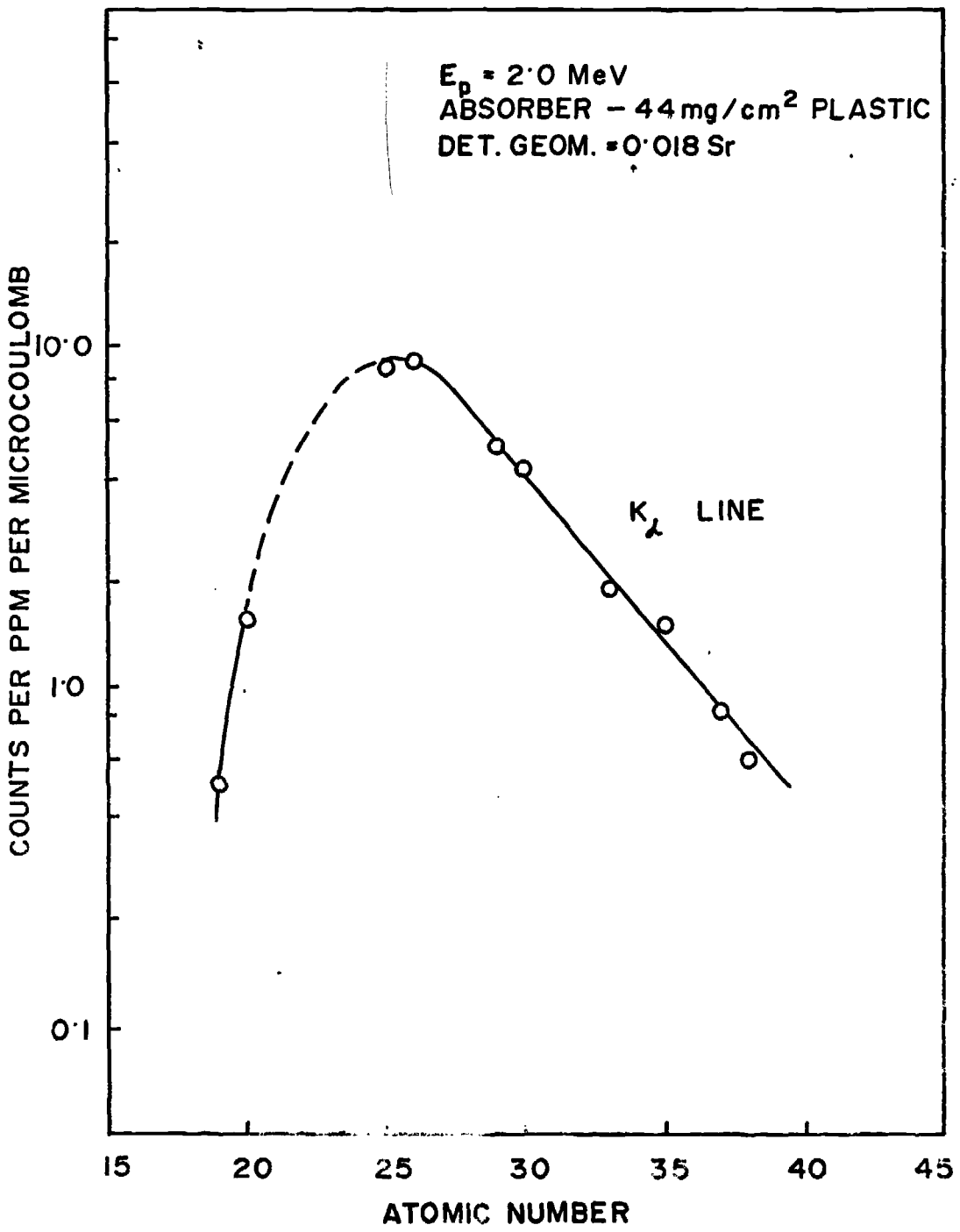
E_p = 2·0 MeV
ABSORBER – 44 mg/cm^2 PLASTIC
DET. GEOM. = 0·018 Sr
K_α LINE
COUNTS PER PPM PER MICROCOULOMB
10·0
1·0
0·1
15
20
25
30
35
40
45
ATOMIC NUMBER

Fig. 3

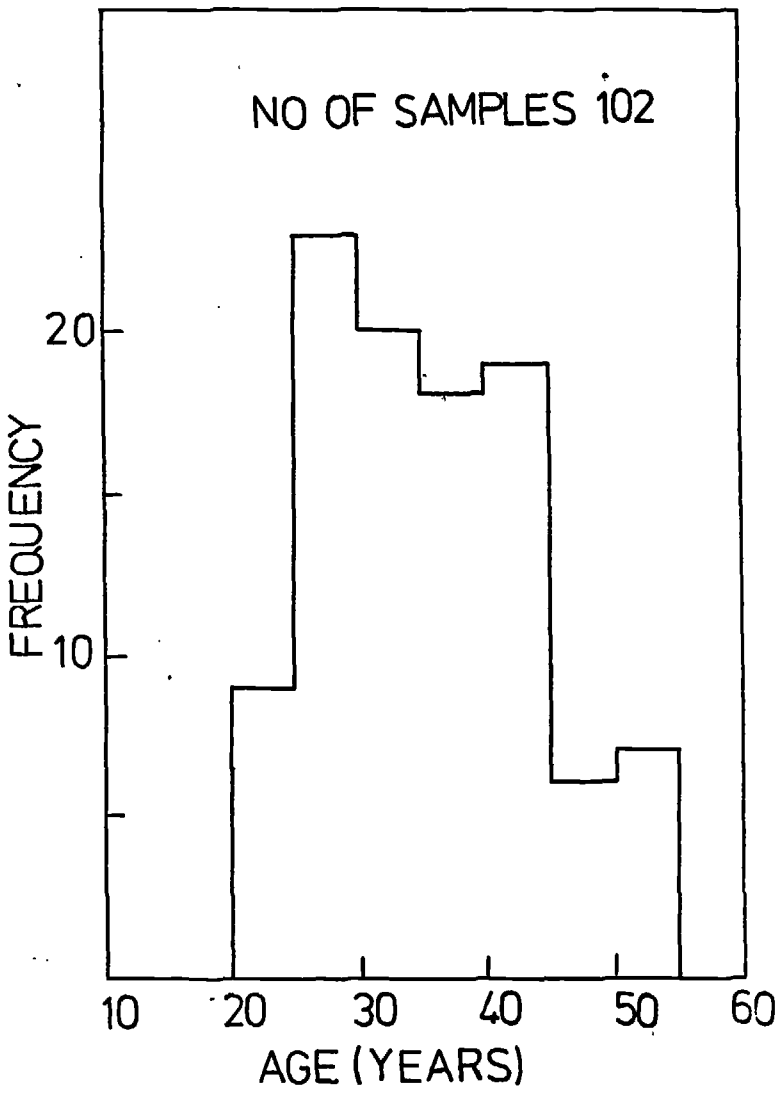

Fig. 4

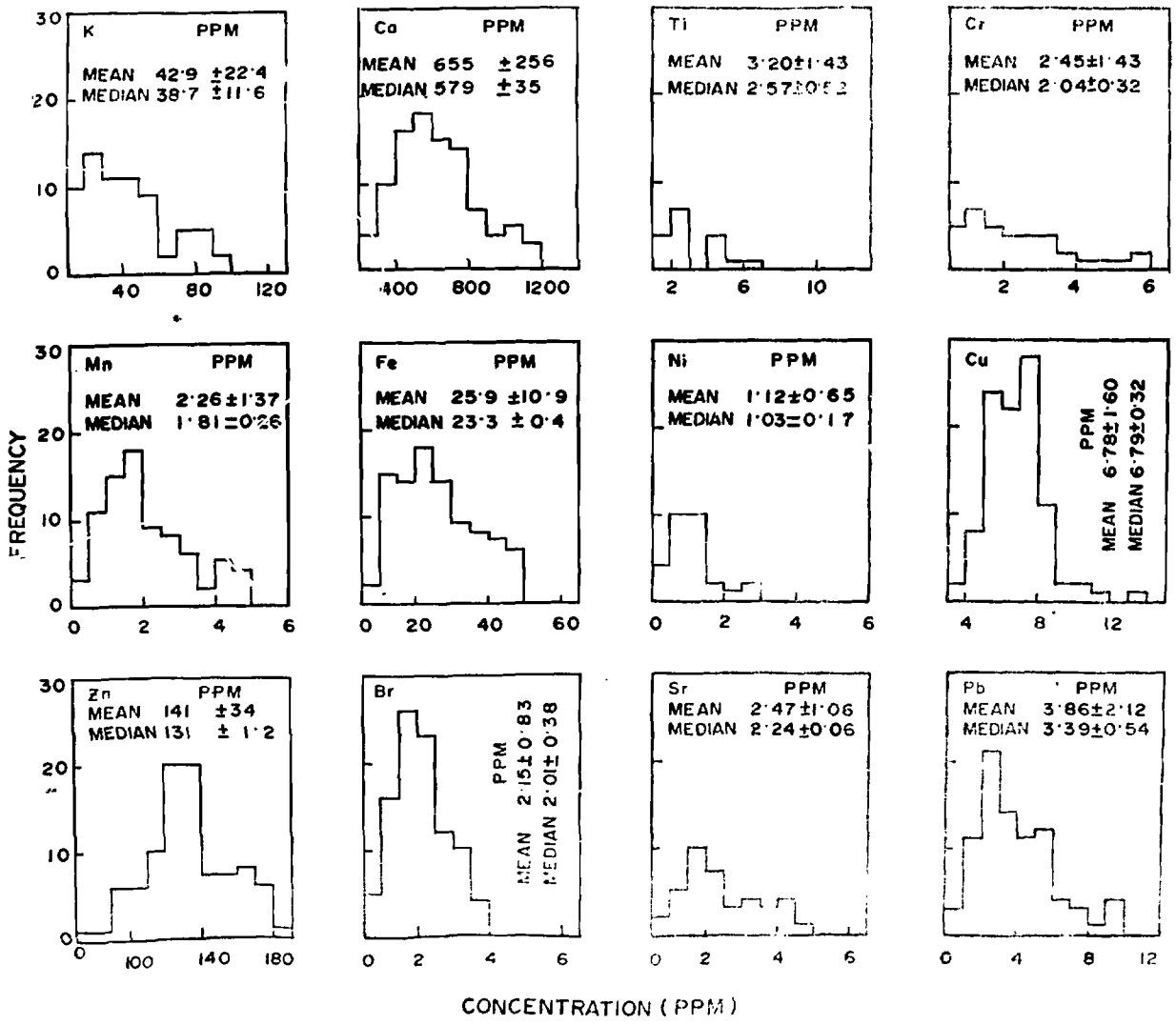

Fig. 5.

...e reported here.