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A study with microbeam PIXE technique needed for the interpretation of data on pollutants in hair obtained with NAA and other bulk concentration analysis, (part of a coordinated programme on nuclear-based methods for analysis of pollutants in human hair)

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CERTIFIED BY:

STUDY WITH MICROBEAM PIXE NEEDED FOR THE INTERPRETATION OF DATA ON POLLUTANTS IN HAIR OBTAINED WITH NAA AND OTHER BULK CONCENTRATION ANALYSIS TECHNIQUES.

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Report of work carried out under
IAEA Research Contract no 2200/RB

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Subject: Study with microbeam PIXE needed for the interpretation of data on pollutants in hair obtained with NAA and other bulk concentration analysis techniques.

Summary: Trace elements in hair can have been introduced through several routes. It is therefore interesting to compare trace element concentrations in the rootbulb with those in the hairparts outside the skin and if possible as a function of the inner position. Scanning micro-beam PIXE analyses over the cross section were carried out with 22 samples of hair from 4 persons selected on the basis of environment or treatment. From 3 persons hair was taken from head, arm-pit and leg and of each type measurements were carried out with one hair at the root and at 1 and 2 cm off the root. Information was obtained about concentration and concentration distributions for sulphur, potassium, calcium, iron, nickel, copper, zinc, lead, arsenic, selenium and bromine. Indications were obtained that Zn, Cu and Fe are mainly deposited in the root through the blood. Of this Zn and Cu distributions are relatively homogeneous. Ca and Br seem to be introduced both through the blood and by other means as perspiration and/or sebum. Pb, As and Se are not found in the root but only in the other parts indicating that only sebum and/or perspiration are involved in their transport. Finally some consequences are given for the reliability of bulk analysis as a tool for finding trace element body burdens or level of outside contamination.

2. Introduction: Human hair is considered as a monitor for the trace element status of a person which includes both internal availability and outside contamination by environmental sources. From the body, trace elements may reach hair through the blood but not only in a straight way during growth but also in a later stage, i.e., via sebum and sweat (apocrine and eccrine). Environmental pollutants of inorganic nature will influence the hair's trace element concentration through entrance in the body but also by direct contact of the hair with contaminated air (fumes, dust) and water (industrial wastes). In this respect it is interesting to note that hair can take up elements from aquous solutions by a mechanical swelling proces as well as by diffusion and chemical bonding through active groups (SH, NH_2) of the proteins. In contact with water elements can also be washed out. Rates of penetration into and desorption from the hair strongly depend on the type of element and physical properties (i.e. pH) of the washing liquid [1,2]. Therefore, one has to accept that trace elements present in either sebum or sweat or in deposited particles, the latter in combination with water or sweat, will penetrate to various extents into the hair. This is also true for trace elements present in shampoo's, coldwave agents, dyeing liquids etc etc.

As sweating but also washing and treating with agents are habits of rather personal and incidental nature, also depending on type of work and clothing, one should conclude that the concentrations of trace elements in hair measured as an average in a bundle of hair strands of varying lenghts (i.e. varying ages) cannot easily be a precise monitor for the internal trace element status nor for the amount of external contamination of a person. For such use it should be necessary to discriminate - if possible - between trace element concentrations present before and after the moment that the hair has come in (direct or indirect) contact with the atmosphere. Being aware of the structure of the hair's follicle one should conclude to the measurement of the trace elements in the lower part of the hair's root (bulb) which has not yet grown out of the "inner sheath". Such a measurement carried out on one single hair is not easily done by one of the well-known trace element determination techniques such as neutron activation analysis (NAA) though a technique indicated by Smith [3] would make it virtually possible for elements present in not too low concentrations. However, another possibility can be found in PIXE (particle induced X-ray emission) which is not quite as sensitive as NAA but which makes it possible - by using a scanning microbeam - to measure radial trace element concentration gradients [4] in layers with a depth of approx. 50 µm. This technique has already been applied by us in a case of possible arsenic poisoning [5] and in a few other unpublished investigations [6]. It was the purpose of the present research project to use the microbeam-PIXE technqiue to obtain more insight into the processes involved in trace element incorporation in human hair.

3. Microbeam PIXE technique.

This technique was developed at the UK Atomic Energy Research Establishment, Harwell by Cookson et al. [7] using a proton accelerator but it has recently become available at a number of other research laboratories. At the time of the IAEA grant the Harwell facility was still the only one in operation relatively near to Delft. In the meantime a facility of comparable type has been built at the Institute of Nuclear Physics of the Vrije Universiteit (VU), Amsterdam. It will probably become available in early 1981.

The results reported here have been obtained with the Harwell facility whereas sample preparation was carried out mainly at IRI (Delft) and partly at VU (Amsterdam).

a. Sample preparation. The hair specimen were cleaned by washing according to IAEA standards (acetone, 3 x water, acetone) and cut into 3 pieces each of them containing the positions (root, 1 cm and 2 cm off root) where measurements were planned. They were separately embedded in araldite resin type MY-753[x], used in combination with hardener type HY 951. A particular hair was stretched in the centre of a plexiglass tube my means of caps with a central hole. The hair ends were fixed at the outside of the caps by adhesive tape. The tube was then filled with resin mixture. For hair root samples the hair end was dipped in the araldite by supported tweezers. After hardening the tube was filled up with resin in the normal way. The cylindrical block with inserted hair was roughly cut perpendicular to the hair direction near to the desired position and the two sections were then machined on a

[x] The resin contains 0,5% Cl and a small trace of Fe, K and Br, but no other trace elements.

lathe with an ordinary cutting tool[+]. One side was used for making a microphotograph and the other was used as sample for PIXE analysis. For root samples the part which also contained the rest of the hair was used for PIXE. As there was no special facility to indicate the boundaries of a hair specimen on the scan the strong sulphur signal was originally used for that. However, it was found that the rise of the sulphur signal was not always sharp which motivated the search for an independent monitor for the hair's boundaries. Some research lead to incorporating 100 ppm vanadium in the form of bis[1-phenyl butan. dionato - (1,3)]oxovanadium (IV)[x] in both araldite and hardener before mixing. This technique was ultimately recognized as a valuable independent method (compare Chapter 5) but has introduced some practical difficulties which are not yet completely solved. Some of the measurements on hair samples embedded in V-spiked araldite showed large V-background signals inside the hair which could be interpreted by a penetration of vanadium into the hair during the hardening proces of the araldite, or by a smearing effect over the surface by the tool during machining but also by improper beamfocussing (comp. 3b3). Experiments with solutions of the V-compound indicated the possiblity of the first proces. We have therefore sought for a technique to prevent the penetration of vanadium. Coverage by a thin layer of non-spiked araldite proved to be impossible because hair is virtually not wetted by unhardened araldite mixture. An - at least - provisional solution was found by covering the hair with a thin silver layer by bringing the rotating hair in contact with silver vapour at low pressure for a few seconds[*]. In the experiments

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[+] As an alternative cutting with a microtome knife was used, which could be applied when taking away most of the araldite on a lathe except a cylindrical piece with 2 mm diameter directly around the hair. However, the microtome knife seems to lead to a less smooth surface of the hair (comp. chapter 5).

[x] one of the few soluble V-compounds to be obtained on the market.

[*] For the coverage of Ag the hair was stretched between two clips on the rotating axes of an electromotor. For making a hair root sample one of the clips was replaced by a small circular iron plate (ϕ 4 mm, d = 1 mm) fixed at a distance of 2 mm off the root. A pointed magnet positioned in line with the rotating axis kept hair and roots end straight by attraction of the iron plate.

carried out with such samples a high percentage of good measurements were obtained. However, both Vanadium and silver were not ideal from the point of view of data handling. In the X-ray spectrum obtained by using a 0,0035 mm Mo absorber (see chapter 3c) the V-peak is situated in a position with a rather high background. The silver L α X-ray energy is relatively near to the potassium K - α signals; they are both situated on a strong background gradient so that separation is difficult. However, a more serious effect of the thin layer of solid silver appeared to be an increase of background at all energies at the boundary positions.
Samples of the described type can easily lead to strong backgrounds resulting from charge build-up at all positions in hair and resin. In most experiments this could be avoided by applying (alcohol) DAG on the araldite surface around the hair, with connections to the metal sample holder. However, this DAG was found to contain appreciable amounts of nickel and iron but also between 100 and 400 ppm of Sn, Ti, Zn, Al and Br, which could contaminate the hair or could contribute to the spectrum in case of relatively large halo's of the beam or of secondary fluorescence emission. It was found that the build-up of charge could also be prevented by high-vacuum deposition of carbon from very pure graphite electrodes.

b. Beam quality. The Harwell PIXE facility is able to produce a 7 x 15 μm proton beam which scans with a 500 Hz frequency over a path of adjustable length. A hair has mostly a somewhat oval form. The largest diameter can vary between 30 and 80 μm, the smaller diameter between 20 and 50 μm. In most experiments a scan was made over the longest diameter which means that the scan width of 15 μm covered 50 to 70% of the smallest hair diameter. Larger beam diameters and irregularities in form of the beam could easily lead to a situation in which concentration gradients over the center line are influenced by concentrations in outer parts of the hair or even in the araldite. Therefore, good beam qualities are of high importance. Unfortunately they could not always be obtained[x)]. It could also have been a reason for high vanadium backgrounds wich were sometimes observed in the middle of the hair (compare 3a). A special metal wire sample containing an

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[x] Adjustment of the sample under the beam was not possible by optical means (simple microscope) but is done by selecting the position of maximum counting output.

Fe core of 25 μ surrounded with 20 μ circular layers of Cu and Ni was prepared by electrolysis to check beam qualities.

c. Data acquisition. The scan length is divided in 32 measurement positions. In most experiments the hair diameter covered approximately 20 of these as a scan length of approx. 100 μm was chosen in relation to hairdiameters of the order of 50 to 80 μm. In any of the 32 positions a full X-ray spectrum was recorded covering 0-14 keV. The Si(Li) X-ray detector with a resolution of 158 eV required the availability of 250 channels per spectrum (56 ev/channel) for a spectrum analysis of reasonable accuracy. The necessary data handling equipment (32 x 250 channels) became available at the end of 1979 and still showed some irregularities at the time of the final measurements (January 1980).

The X-ray detector was provided with a 0,0035 mm Mo absorber with a nearly 100% transmission of X-rays with energies > 6 keV (Fe, Ni, Cu, Zn, As, Se, Pb, Br) and acceptable intensity losses for X-rays between 4 and 6 keV (Ca, Sc, V, Cr). A very strong absorption of S-Kα rays (2,3 keV) is necessary to reduce the counts obtained from the approx. 4% orginating from the hair's proteins.

As the detector is situated under an angle of 45^{o} to the beam some geometrical effects can be expected for X-rays originating from deeper layers. It is probably the reason that for the metal wire (Cu, Ni, Fe, N, Cu) cross sectional scan the signals for the left hand part of the scan were lower than those for the right hand side. Irregularities in the surface smoothness could also lead to fluctuation.

The facility was provided with meters for proton beam strength (dose rate) and total dose the latter did not always provide reliable data. Dose rates of the order of 4 μ Coulomb/hr and measurement times of 1 or 2 hours were used leading to maximum total sulphur counts per position in the centre of the hair of approx. 60000. Under these conditions.

a burning effect in the hair is observed but not of a strong nature. Such a burning effect could lead to loss of the elements to be analysed, which was not further investigated.

d. Data handling. The special problem connected with micro-beam PIXE is the fact that per position only a few counts for X-rays of some element are sometimes found on top of a major background. A good analysis should involve an appropriate data handling programme for distinguishing between background and element signals. Two systems have been applied during 1980. At Harwell a system published by Statham [8]was further developed and used whereas parallel to it the same data were subjected to a programme developed at the V.U., Amsterdam [9]. The Stratham technique does not use a continuous background of standard form but makes subtractions in several steps so that the background in channels at both sides of the peak show a zero average. The result can be that resulting peak areas are found negative. The V.U. technique makes use of a standard background shape. Negative peak areas after subtraction are indicated as zero. The results are separately shown in appendices I - III and IV - VI. The data were in all cases standardized on one hair diameter and on a total count yield for vanadium in the resin of 55 which in many cases coincided with a total dose of 1 μ Coulomb. By using estimates for counting efficiency of the detector with absorber as a function of X-ray energy and for the PIXE cross sections of the various elements (see table I) an indication about the absolute trace element concentrations could be obtained by comparison with the vanadium concentration of 100 ppm in the resin[x)]. However, it should be borne in mind that the poor statistics of the low signals but also some limitations of the equipment and the data handling programmes make these data not very accurate. On the other hand the conclusion can be drawn that the obtained data are certainly within the ranges for trace element concentrations in hair as described in the literature.

4. <u>Selected hair samples</u>. In this part of the research only a few hairs could be analysed. They are described in table II. Hair B was an example of hair from a period of lower industrial activities with limited chances of external contamination. Only little cuttings of hair were available resulting from regular haircuts [10]. Hairs C, D, E were taken from a professional leadsmelter in a small battery producing firm. At the time of the hair sampling only a few physiological data were known: δ-aminolevulinic acid (ALA) in urine 8.5 mg/l (normal-0-5.4), haemoglobin in blood 8.8 m mol/l (normal 9.5-10.5) indicating only a minor lead intoxication in accordance

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x No corrections were made for differences in penetration depths in resin and hair.

van Zw. van Zw. van Zw.

with weak health complaints. Total Pb contents of single hairs were measured by PIXE (VU Amsterdam) as a function of distance from the scalp (see Table III). These hairsamples were taken complete with rootbulb and they provide the possibility to distinguish between hairs from different body parts (head, arm-pit, leg) with different contributions of sweat and outside contamination and also to compare distributions at different positions along the hair including the bulb.
Hairs F, G, and H were taken from a farmer living on Terschelling, one of the North-Sea islands, without industry and with only very limited gasoline motor traffic. Again influence of the location on the body and of the position along the hair could be investigated.
Hair I was taken from a patient to whom As-containing drugs had been administered. Earlier NAA analyses [2] had shown that a strongly increased As-content (70-80 ppm) was present in the first 3 cm.

5. Conclusions

A Attention is first focussed on the data obtained for the hairs of persons van Zw. (Samples FI, II, III, GI, II, III, HI, II, III) and AP (sample B) (compare appendix I). They seem to be comparable to a certain extent as outside contamination is not expected in both types of hair. There is indeed a strong similarity apart from the fact that A.P.'s hair clearly shows an increased lead concentration, estimated to be of the order of 4 ppm as compared to 1 ppm found in the various measurements of van Zw.'s hair. These data should be compared with those found at the present time in various communities. For rural areas in Canada and the USA concentrations between 4 and 25 ppm appear to be normal [11, 12] and our data seem to confirm that such increased values are the result of contamination by lead from the high-octane fuel used in motorcars. In contrast to them the moderately increased lead content in A.P.'s hair should rather be attributed to the use of lead tubing for water distribution. It is impossible to make conclusions about the position of the lead in this hair, though it does not seem to show preference for deposition at the hair's boundaries.
When comparing the sulphur signals found for the various samples the unsymmetric distribution over the hair is very distinct. Only in four runs (135-138) a more flat signal level comparable to those found in earlier work [5] was found. The strong maximum at the left hand of the scan cannot be the result of the sideway position of the X-ray detector as can be deduced from measurement of the metallic check sample. There is a possibility that the peculiar shape is related to the use of a microtome knife which could have a shoving action as well. Indeed the microfotographs

van Zw. van Zw. Person: A.P. (1904)

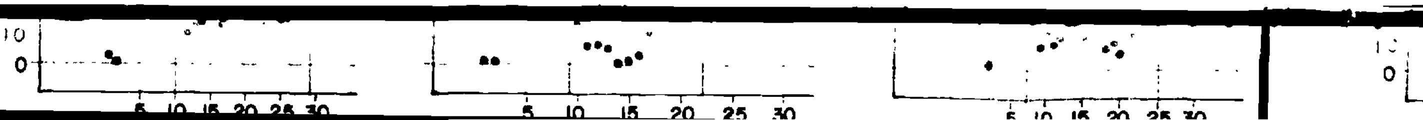
indicate the presence of parallel wrinkles. However, if this true a successive removal of about 1 mm of the surface with a tool on the lathe seems not always be able to correct the damage. Therefore, one should keep open the possiblity that the sulphur distribution in hair can be inhomogeneous due to natural causes and - in more distal regions - to partial decomposition (hydrolysis) of the hair. A second observation is the presence of a dip in the S-signal in the centre, which has been found before [5] and which is probably related to the presence of a medulla [compare 13] in certain hairs. A third observation involves the height and width of the sulphur signal. The height in most measurements is situated between 5000 and 8000 counts (standardised on 55 counts of Vanadium). In the highly unsymmetrical scans discussed before maxima of 10.000 counts are found. However, in the two rootscans (runs 137, 138) there is a distinctly lower signal i.e. of the order of 2000 counts. Moreover, in those two the S-signal does not rise at the hair's boundaries which are clearly indicated by the stepwise change in the V-signal but at a more inner position.

These findings are in line with literature [13,14] which tells that hair formation in the bulb (root) starts with formation of a protein with a lower S-content but a relatively high concentration of -SH groups. This happens only in the center (cortex) indicating that outer regions of the bulb have a different nature. Some of the microphotographs indeed show a different structure. At a higher level of the follicle another protein containing more sulphur is synthesized. Somewhat later in the growing process (about one third up the follicle) the first mentioned proteins are longitudinally directed and mutually bounded by oxidation of-SH groups to -S-S-groups. After this keratinization which starts at the outside (cuticle) and progresses inside (cortex) the hair can be considered dead. Uptake of trace elements through the blood must be restricted to the above described lower one third of the hair's follicle (3 times the length of the bulb) as no blood vessels are present above that position. The trace element data obtained for the three rootsamples (runs 137, 138, 142) indicate that the elements Ca, Fe, Cu, Zn, Br are already introduced in this phase: For K, Ni, Pb no conclusions can be made from these measurements.

When comparing the results of the various runs one can conclude:

a. there is no fundamental difference in concentration levels of Zn, Cu, Fe between roots and rest of hair nor between the various types of hair (head, arm-pit, leg).

b. The Zn, Cu, Fe concentrations show rather homogeneous distribu-



tions with superimposed peaks mostly near the hair boundaries. Contributions of the superimposed peaks seem to become stronger in the sequence Zn, Cu, Fe. The peaks for Fe can be relatively strong and will probably influence the average concentration. This is in agreement with older measurements [5]. These data seem to indicate that most of the Zn, Cu and Fe is already introduced through the blood during the early stage of hair formation. Then one would expect a reasonable steady bulk concentration in hair for at least Zn and Cu which has been confirmed for Zn by many authors but also for Cu by some authors [10]. About the reasons for the occurrence of the peaks no conclusions can be drawn, they are both observed in root samples as in hair at several centimeters off the root.

c. Ca and Br distributions are very irregular and are sometimes high in the center of the hair. Such distributions were found for As^{III} [5] and appear to be typical for elements which are not bound to active groups of the hairs proteins and are easily washed out in a later stage. On some samples (AP, run 159) the Ca also shows peaks at the hairs boundaires [compare 5].

B Most of the conclusions drawn above are confirmed in the series of samples of person B (samples CI, JI, JII, DI, JI, JII, EI, JI, JII, compare appendix II).

Special attention should only be given to Br, some single data of Ni and Cu and of course Pb. As compared to the samples described under 5A the bromine concentration in these hairs are rather high especially in hair parts 1 and 2 cm off the root and only in head hair and arm-pit hair but not in leg hair. This seems to indicate an extra deposition of Br through perspiration which seems also to lead to increased concentration at the outside. Nickel for which no indications are found in most hair seems to be present in sample EIII (run 155). With respect to Cu an extremely high concentration was found in DII (run 146) which indicates an extra Cu-deposition through a different route. For Pb the results are extremely interesting as no indication of any lead are found in the roots but only in the hair parts which have grown outside the skin. In these latter cases the lead is present at the outside except in arm-pit hair DII (run 146). One tends to conclude that Pb in contrast with Zn, Cu, Fe is not introduced through the blood but through other routes. A problem in the interpretation is the limited physiological information. The man in question is supervisor of an open leadsmelting unit and will certainly have been in contact with lead vapour. However, there is not a very high concentration found in head hair but this is found in arm-pit hair which suggests that perspiration plays a role perhaps only in the redistribution of outside contamination. Unfortunately the series of arm-pit hair is not complete which makes it impossible to see whether the deviations in height and form of Cu and Pb distributions in run 146 are mere coincidence or not. More insight can only be obtained by comparing these results with those for hair of other persons with more strongly deviating physiological properties. The absolute concentrations calculated from the PIXE data are certainly lower than those found by bulk analysis (Table III). It might mean that Pb-concentrations can fluctuate strongly on the scale of a few hundred microns as is the case for As (see 5c). From results of washing with HCl (Table III) the impression is obtained that part of the head (comparable to what is found by PIXE) is more strongly bound.

C The data obtained for the hair of a patient who had taken an As-containing drug (JI, II, III) are shown in appendix III. Conclusions with respect to S, K, Ca, Fe, Cu, Zn are fully comparable to those drawn in chapter 5A. For Ni there is again a single example of increased concentration in J II (run 157). In the presence of As, Pb and Br some difficulties arise in the interpretation of combined peaks (As-Kα + Pb-Lα, 10.54 keV; As-Kα + Br-Kα. 11.87-11.92 keV). A separation can only be carried out on the basis of Pb-Lβ and Br-Kβ single peaks. As a result the calculated signals for Pb-Lα, AsKα, and Br-Kα are less reliable. Therefore, it is better not to discuss the data for Pb and Br involving only little counts which will not interfere too much with conclusions concerning the arsenic distributions. Here again (compare Pb) no As is found in the hair's root but only at places which have grown out of the skin. In sample J II (run 157) strong peaks are found at the outside and the average As-content over the hair is not fundamentally different from the bulk value of 70-80 ppm found earlier by NAA. In sample J III (run 158) a comparable distribution pattern is found but on a much lower concentration level. This seems to be in contradiction with the bulk analyses mentioned above [2] where lower As-contents (approx. 10 ppm) were only found at regions more than 3 cm off the root. However, Smith [15] has already shown that therapeutic doses of As lead to strong variations (factor 6 or more) in As-content even between joining sections of 1 mm. He also shows that As-contents resulting

from outside contamination show smaller variations. When considering the various possible routes apart from the blood which does not seem important for As deposition in hair, the eccrine sweat might be compared to an outside contamination with a rather large area of action. The strong concentration variations on a 50 μm (and 1 mm) scale would then point to either sebum or apocrine sweat as a transport carrier.
The measurements of the J-type hair samples further show exceptional results for Se. The concentration is again very small in the root bulk but is very strong in general and predominant at the outside for the other samples. Again one gets the impression that Se is not introduced through the blood but by some other route. More measurements are necessary to make conclusions about the concentration variations over smaller lengths. Furthermore, the question arises why the selenium content of this hair is so strongly increased, as this patient was not mentioned as having received Se-containing drugs as well. But many possibilities arise including washing with Se-containing shampoo.

The various measurements though they are only of a preliminary nature have shown that scanning microbeam PIXE research can provide much important information about concentration variations over length and diameter of the hair. Much more work including the development of proper sample preparation techniques is necessary for reaching a good understanding of the mechanisms responsible for the introduction of trace elements in hair. So far it appears that bulk analyses are only indicative for Zn and Cu also because outside contamination of the hair by these metals is not very probable though for Cu the measured hair length should be limited to a few cm's as there is an easy uptake of Cu from very low concentrations in water [1, 16]. For Fe only the inner concentration seems useful as an indication of the internal status which means that radial scans by microbeam PIXE are necessary. The same could be true for Ca. For Pb, As, Se it is relatively easy to find increased levels by any bulk analysis, but it appears difficult to distinguish between effects of internal status and outside contamination by using radial PIXE scans because both effects will lead to increased concentrations at the outer hair's wall and no information can be obtained from the rootbulb. There is still a chance that something can be learned from the upper part of the hair's follicle if one can find a technique to distinguish between that part and the outer region of the hair. More research - if possible with thin slices of 20 μm thickness - could give more information. For Br no conclusions can yet be made with

respect to the best way of obtaining information concerning the body status, but is is probably not a very important element in that respect. Finally, there are of course a number of important elements of which no information is obtained. In some hair specimen indications are found for P(Kα), Cd(Lα), I(Lα) and Hg(Lα) but they have not been computed because their X-rays are situated on either the shoulder of the sulphur peak or on the high bremsstrahlung background. It seems useful to search for Kα signals of Mg, Cl, Cr, Mn, Co, Rb and Lα-signals of Mo, Sn, Sb and W in further work.
Finally, one special result is worth rementioning i.e. the fact that no fundamental differences seem to be present between trace element concentrations of head, arm-pit or leg hair. The differences claimed by some investigators must be merely a result of secondary effects.

This report is not finished without mentioning the highly appreciated cooperation with Dr. J.A. Cookson (UK, AERE, Harwell), Dr. P.S. Tjioe (IRI, Delft), Dr. R.Vis and Mr. A. Bos (V.U. Amsterdam).

Table I

PIXE cross sections (σ), X-ray transmission coefficients ($\varepsilon = {}^{I}/_{I_o} = e^{-\mu\alpha}$) and relative concentration coefficients relative to V(p) for 3 MeV protons and 0.0035 mm Mo absorber.

Element (M)	E_M (keV)		$\sigma_M^{+)}$	$\varepsilon_M^{x)}$	$p = \frac{\sigma_V \cdot \varepsilon_V}{\sigma_M \cdot \varepsilon_M}$
Ag	3,05	(Lα)	1092	0,0093	3,658
K	3,31	(Kα)	543	0,0106	6,455
Ca	3,69	(Kα)	446	0,0226	3,686
V	4,95	(Kα)	258	0,144	1,0
Fe	6,403	(Kα)	146	0,359	0,709
Ni	7,477	(Kα)	97,6	0,545	0,698
Cu	8,046	(Kα)	78	0,580	0,821
Zn	8,637	(Kα)	64,2	0,628	0,921
Pb	10,55	(Lα)	53,8	0,757	0,912
Br	11,92	(Kα)	21,2	0,803	2,18
As	10,54	(Kα)	33,0	0,757	1,49
Se	11,22	(Kα)	27,0	0,776	1,77

Concentration of element M = $\frac{N_M}{N_V} \cdot p \cdot 100$ ppm (N is no of counts)

+) Johansson et al., Nucl. Instr. Meth. 137 (1976) 473-516

x) Storm, Israel, Nucl. Data Tables 7 (1970) 1

Jenkins, de Vries Practical X-ray Analysis.

Table II

Selected hair samples

Sample	Person	date of sampling	date of birth	part of the body	part of hair analyzed				details
					unknown	root	1 cm off root	2 cm off root	
B o)	A.P.	1904	1898	head	B	--	--	--	ordinary citizen male
C	B.	Oct. 1978	1941	head	--	C.I	C.II	C.III	lead smelter, male
D	"	"	"	armpit	--	D.I	D.II	D.III	
E	"	"	"	leg	--	E.I	E.II	E.III	
F	van Zw.	Nov. 1978	1950	head	--	F.I	F.II	F.III	farmer of area remote from industry and traffic, male
G	"	"	"	armpit	--	G.I	G.II	G.III	
H	"	"	"	leg	--	H.I	H.II	H.III	
J x)	patient	--	--	head	--	J.I	J.II	J.III	administered 56 mg As/day during 80 days, male

o received from Miss. R. Cornelis, see [10]

x received in 1967 from Dr. J.M.A. Lennihan, Glasgow, see [2]

Table III

Bulk Pb-contents measured in single head hairs of B.

by means of PIXE

Hair	Treatment	total over 10 cm length	Per cm length counted from scalp				
			1st x)	2nd x)	3rd +)	5th +)	6th o)
1	IAEA stand. wash	57	--	--	--	--	--
2	"	--	263	113	--	--	--
3	"	--	--	239	125	--	--
4	" + 0.1 N HCl 1 day	--	695	100	361	137	390
5	" + 0.1 N HCl 5 days	--	90	23	10	35	168
6	ultrasonic in water	--	77	20	8	--	--

x PIXE analysis of nondestructed hairpiece, impregnated by Ce standard, placed on foil, irradiated sideways with approx. 3 mm beam; calculated max. error in case of non-homogeneous distribution of either Pb or Ce is approx. 23%

+ PIXE analysis of hairpiece destructed by conc HNO_3 (3 drops) and H_2O_2 (2 drops) in teflon container under infra-red lamp, till dry, treatment repeated, dissolved in standard Y-sulfate solution, deposited on foil.

o same as +) except Na_2SeO_3 standard.

Literature

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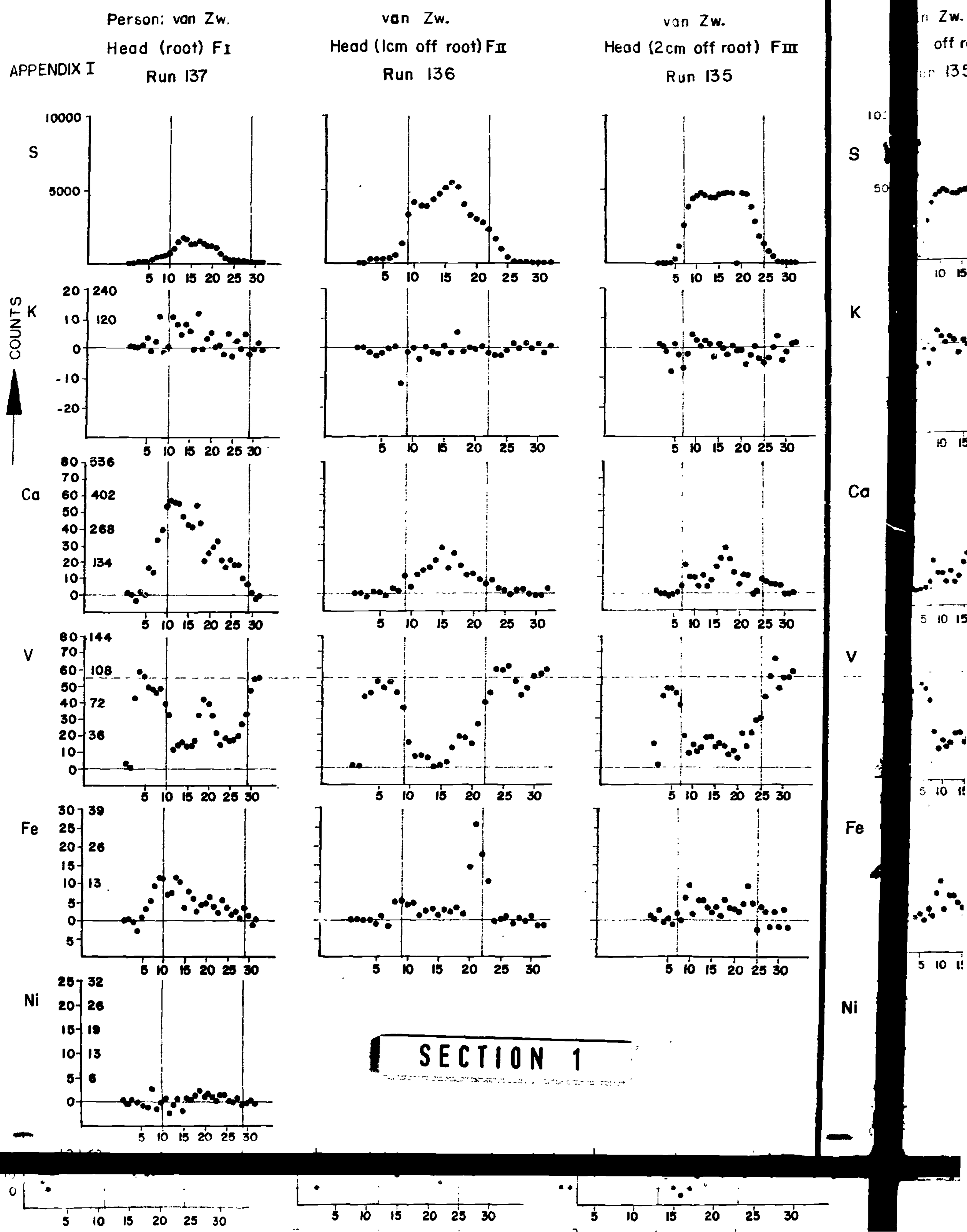
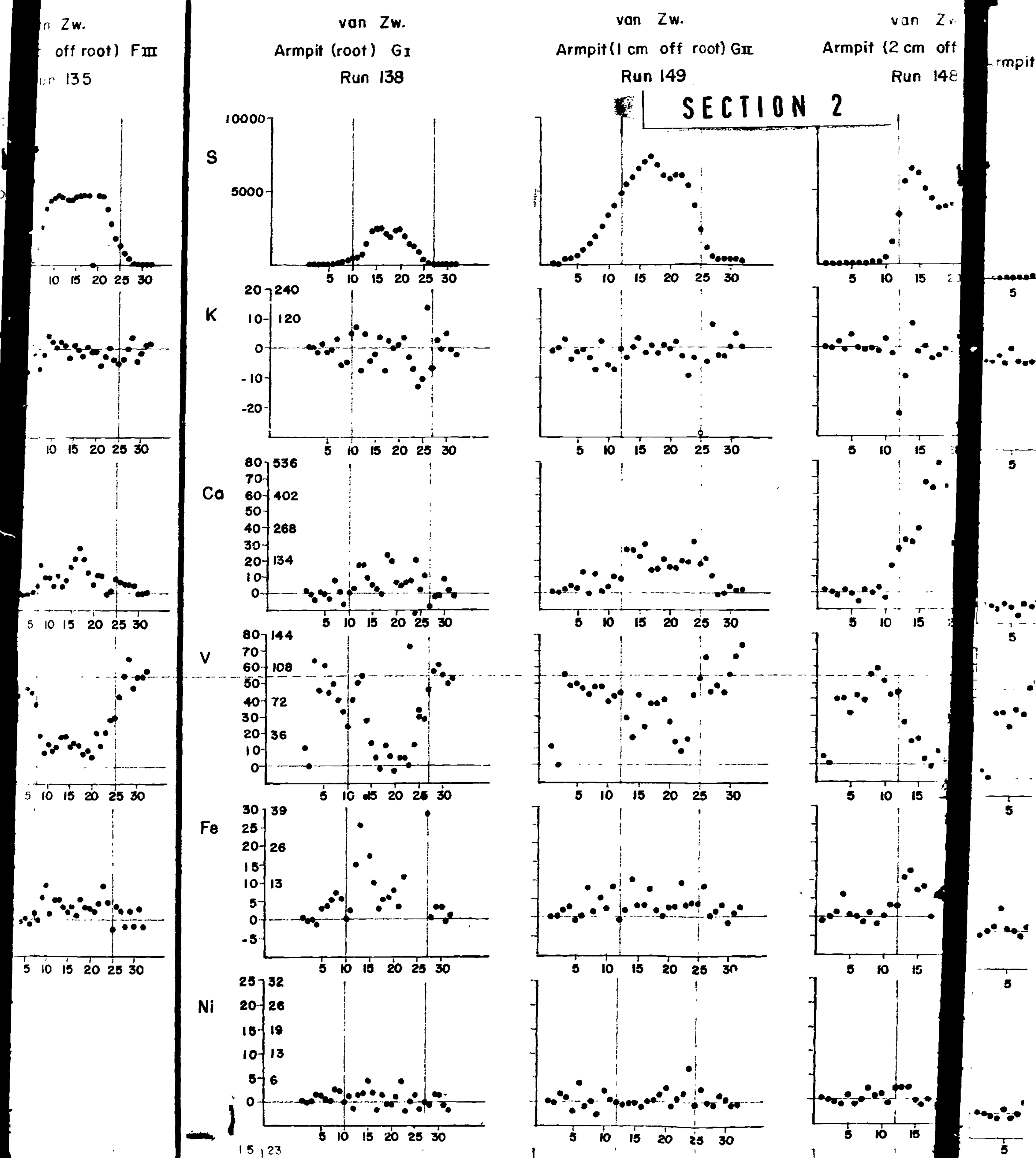
Appendix I

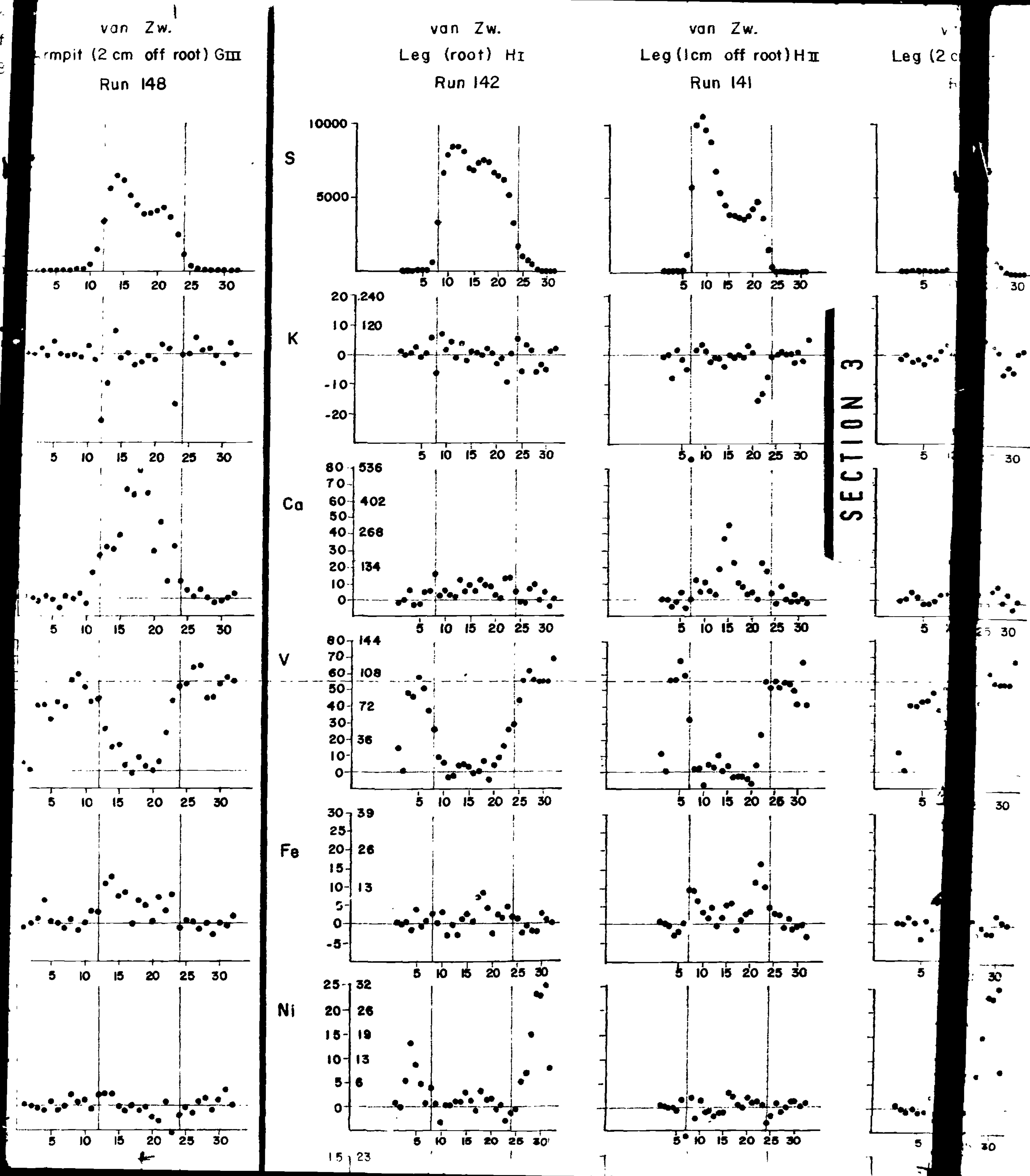
APPENDIX I


Person: van Zw.
Head (root) FI
Run 137
van Zw.
Head (1cm off root) FII
Run 136
van Zw.
Head (2cm off root) FIII
Run 135
S
K
Ca
V
Fe
Ni
COUNTS
SECTION 1

SECTION 2

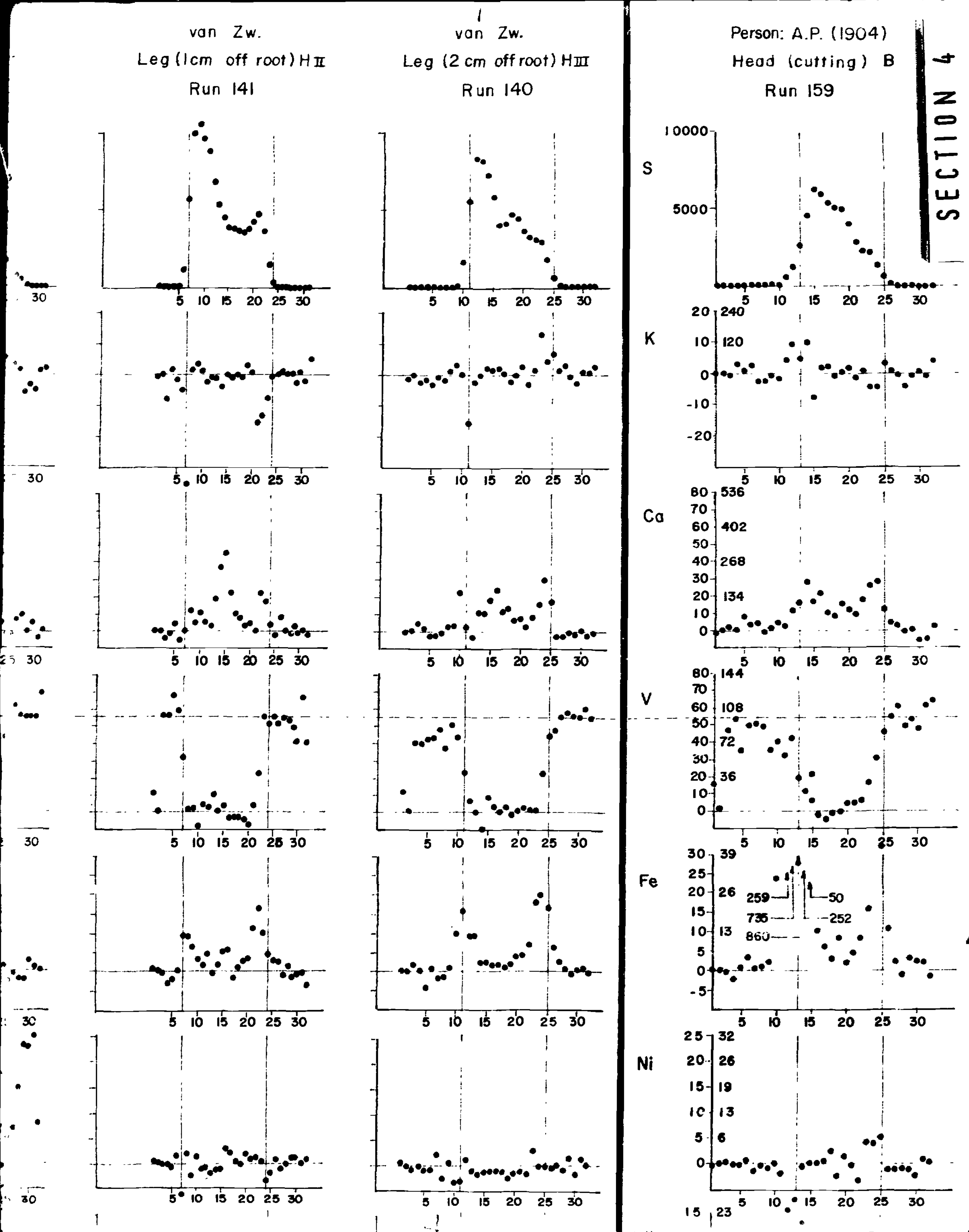


n Zw.
off root) FIII
Run 135
van Zw.
Armpit (root) GI
Run 138
van Zw.
Armpit (1 cm off root) GII
Run 149
van Zw.
Armpit (2 cm off
Run 148
rmpit
S
K
Ca
V
Fe
Ni
10000
5000
20 240
10 120
0
-10
-20
80 536
70
60 402
50
40 268
30
20 134
10
0
80 144
70
60 108
50
40 72
30
20 36
10
0
30 39
25
20 26
15
10 13
5
0
-5
25 32
20 26
15 19
10 13
5 6
0
5 10 15 20 25 30

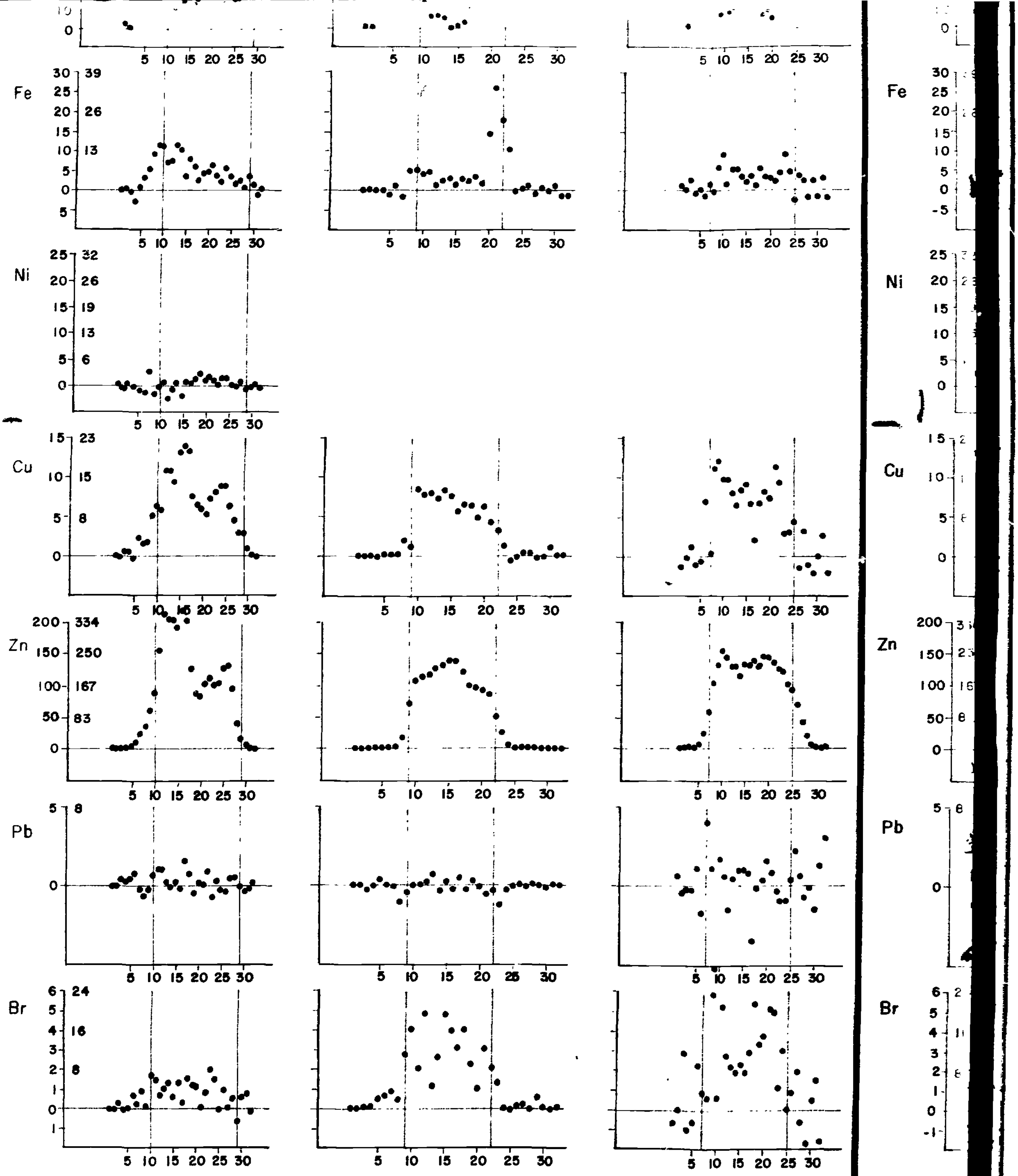


APPENDIX III

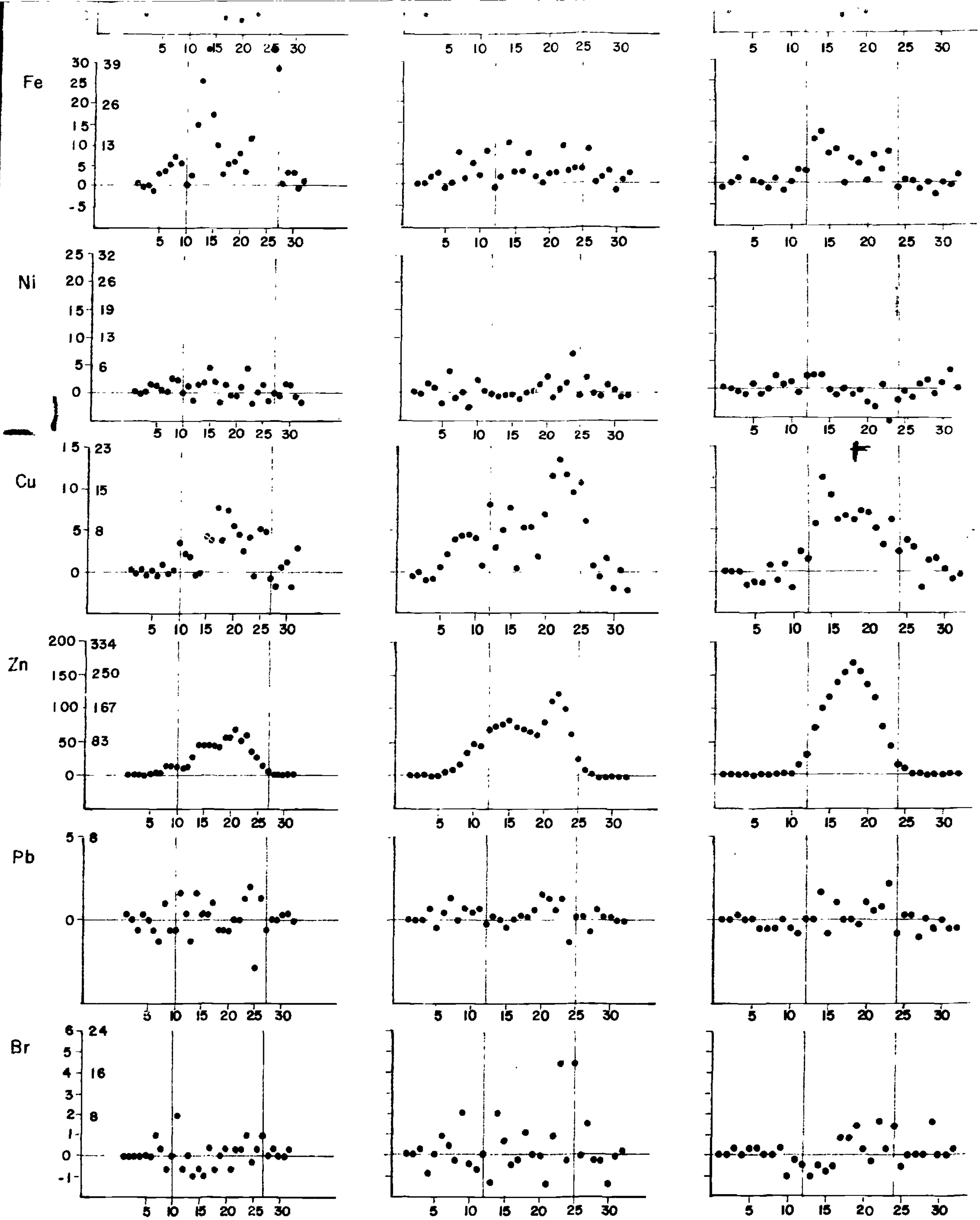
PATIENT of ALEXANDER / LENIHAN



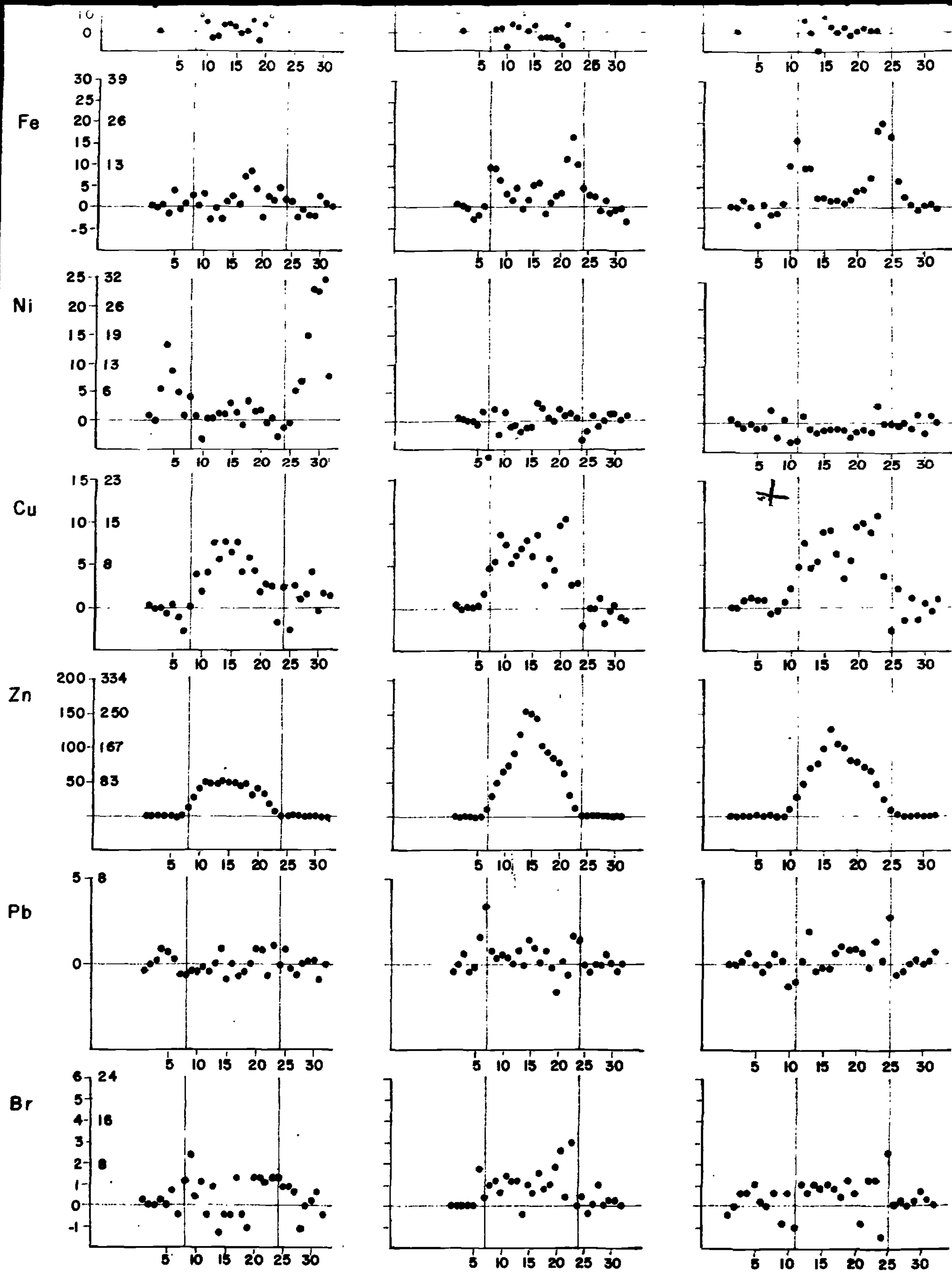
van Zw.
Leg (1cm off root) H II
Run 141
van Zw.
Leg (2 cm off root) H III
Run 140
Person: A.P. (1904)
Head (cutting) B
Run 159
SECTION 4
S
K
Ca
V
Fe
Ni
10000
5000
259
735
860
50
252



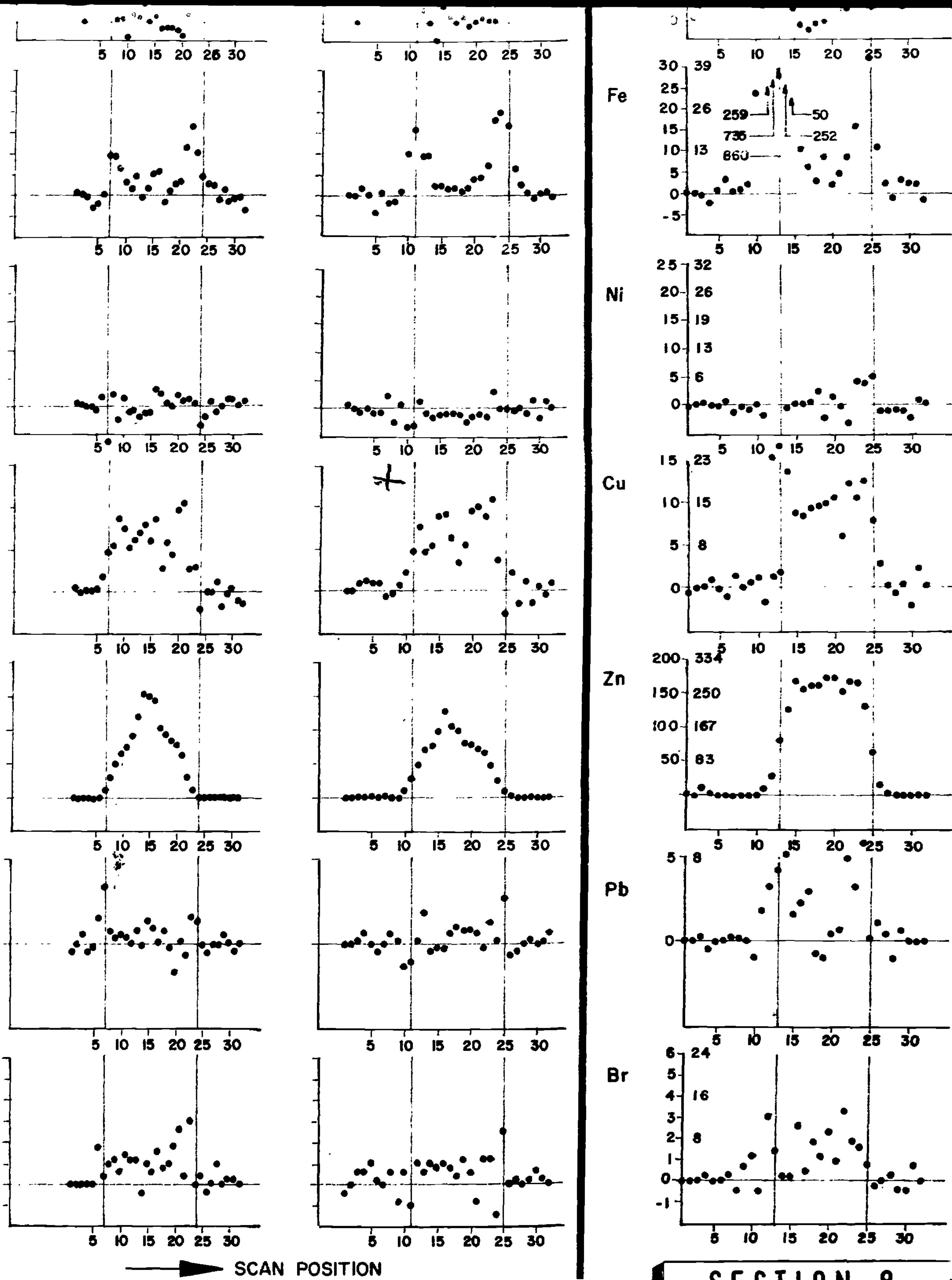
SECTION 5



SECTION 6



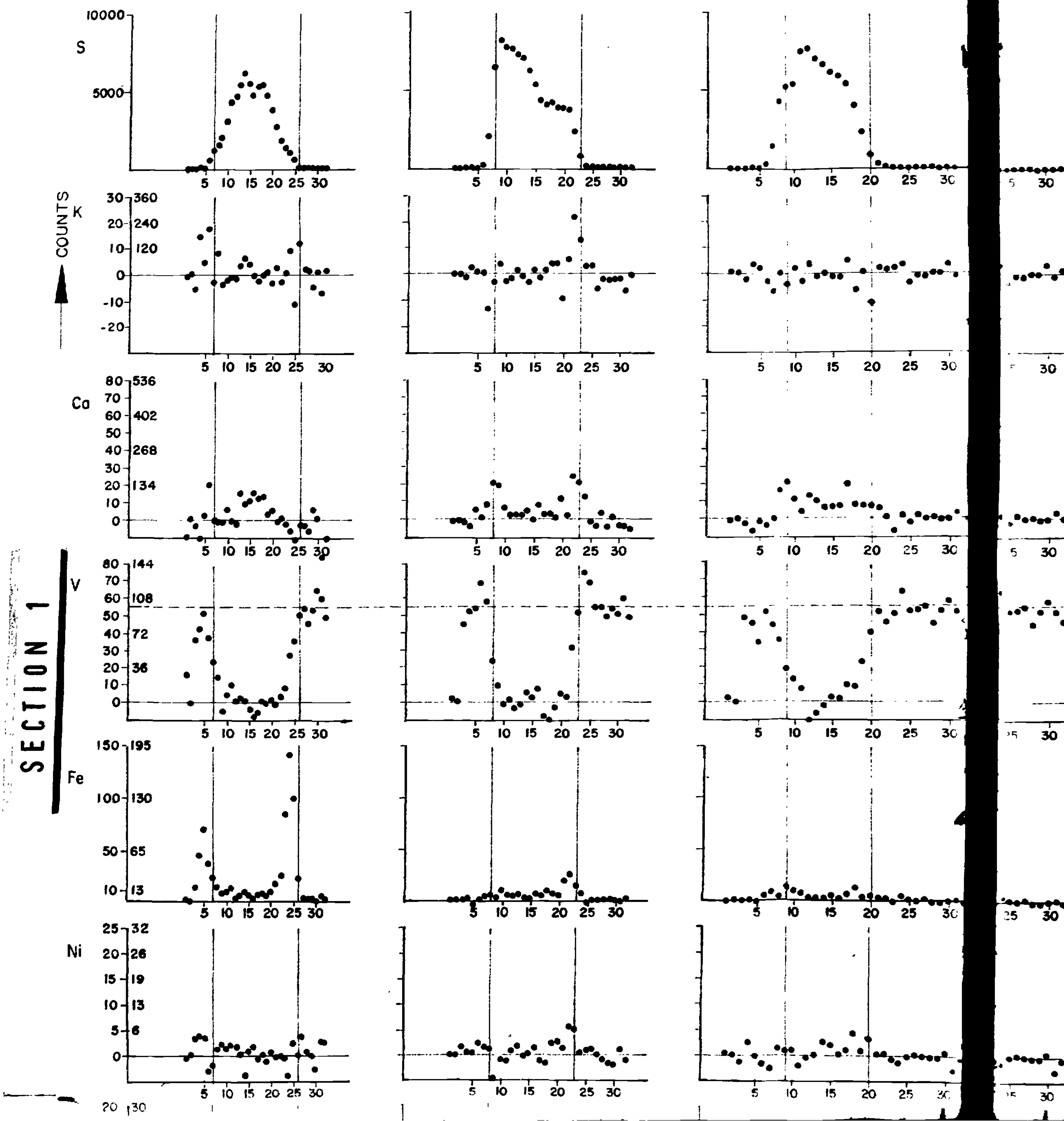
SECTION 7 ——► SCAN POSITION



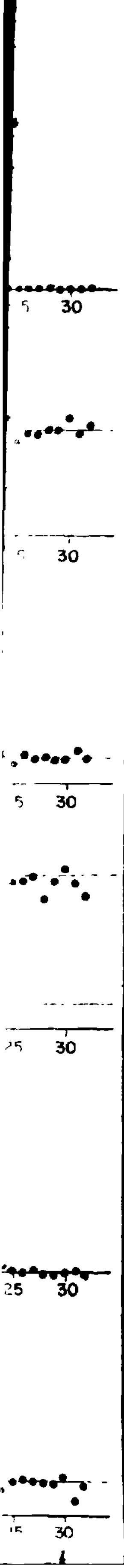
SECTION 8

APPENDIX II

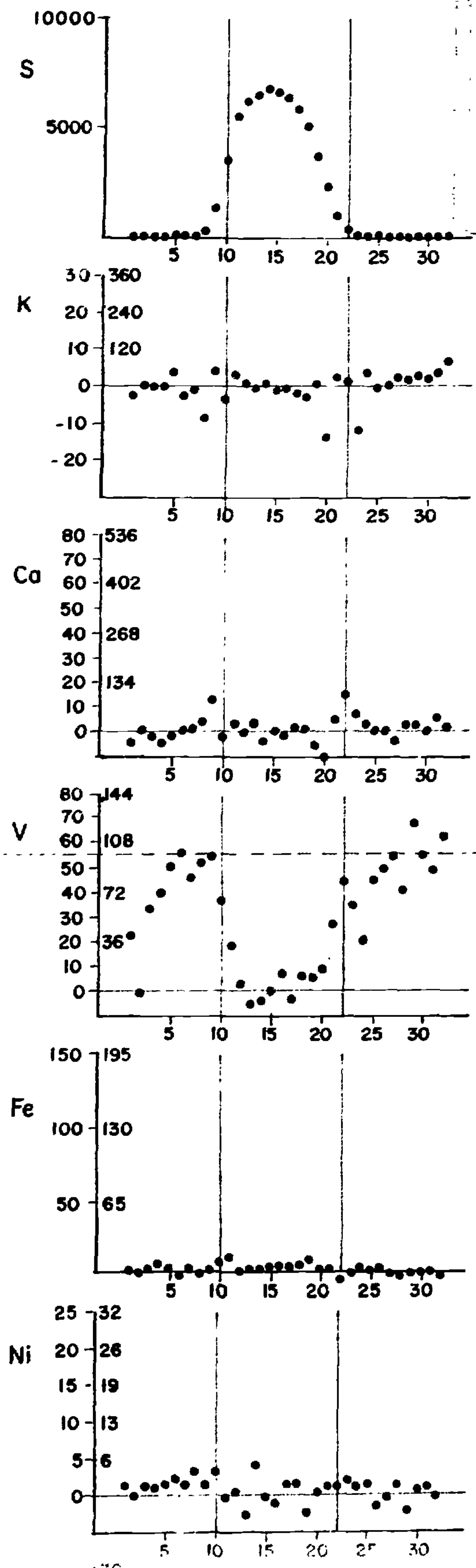
Person: B. Head (root) CI Run 150 | B. Head (1 cm off root) CII Run 144 | B. Head (2 cm off root) CIII Run 145 | CIII



C III

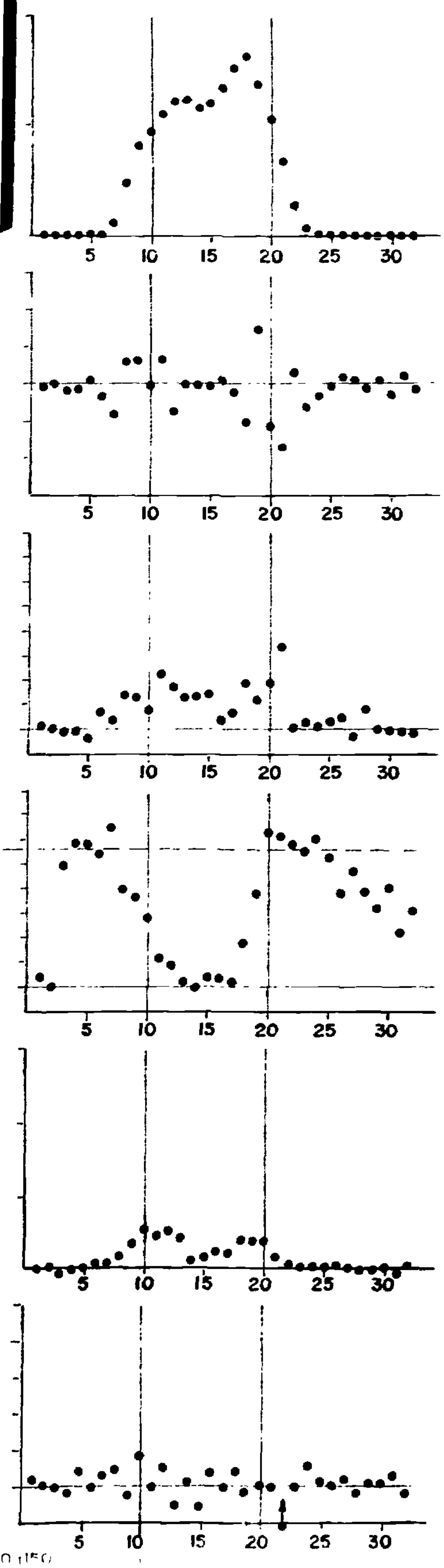


B.
Armpit (root) D I
Run 151

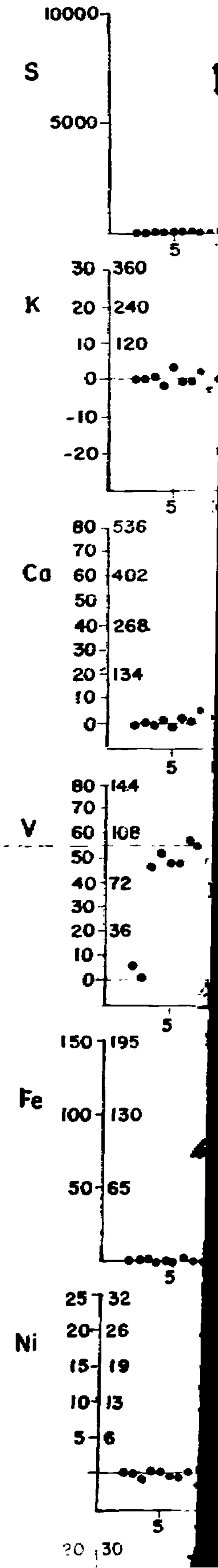


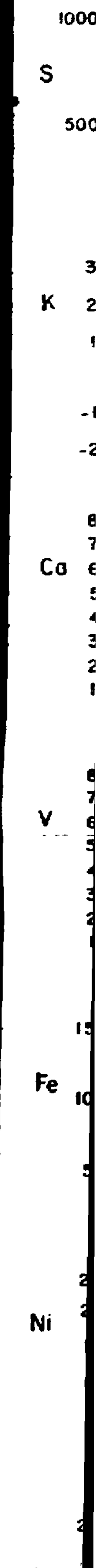
SECTION 2

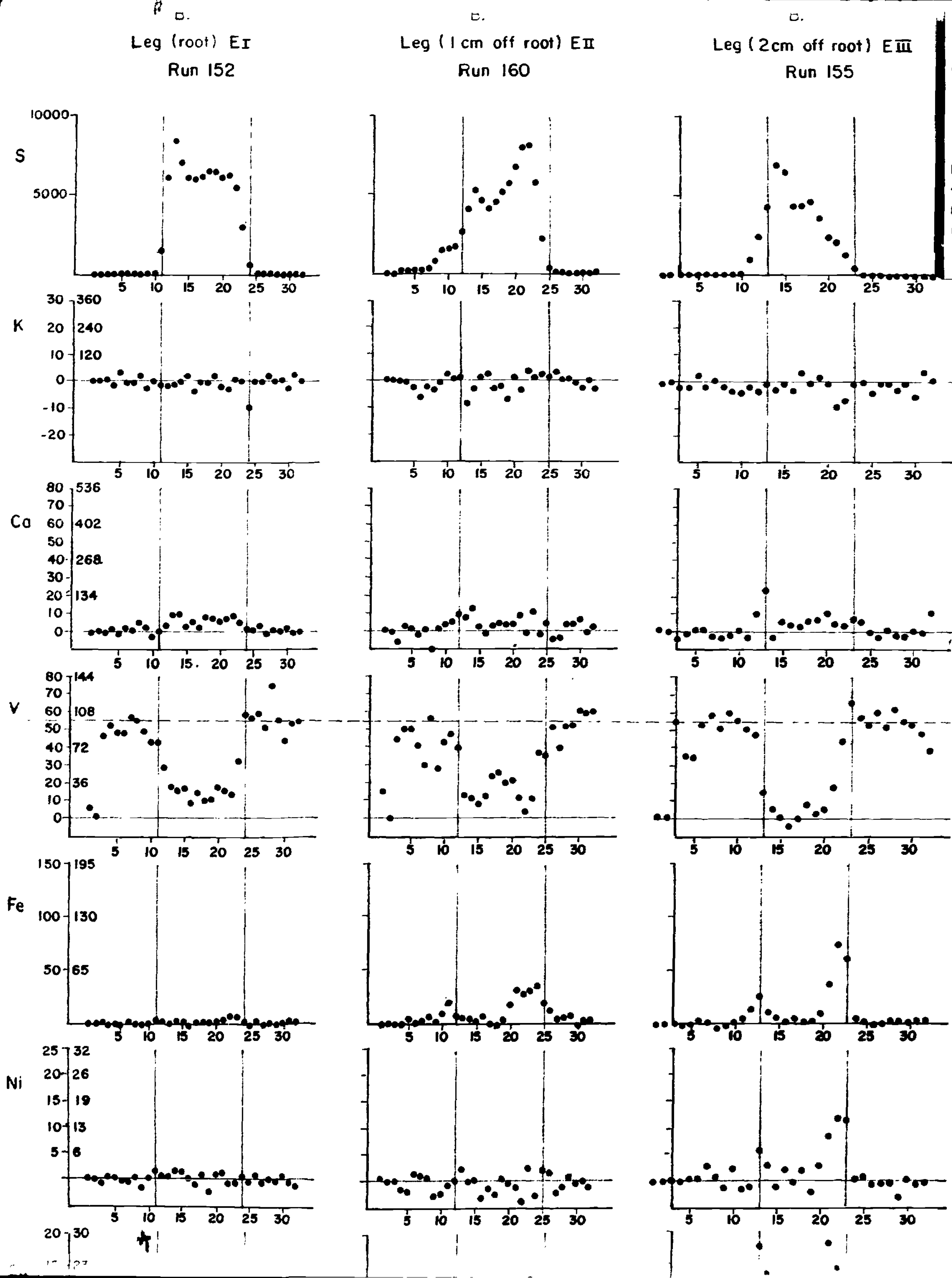
B.
Armpit (1 cm off root) D II
Run 146



Le

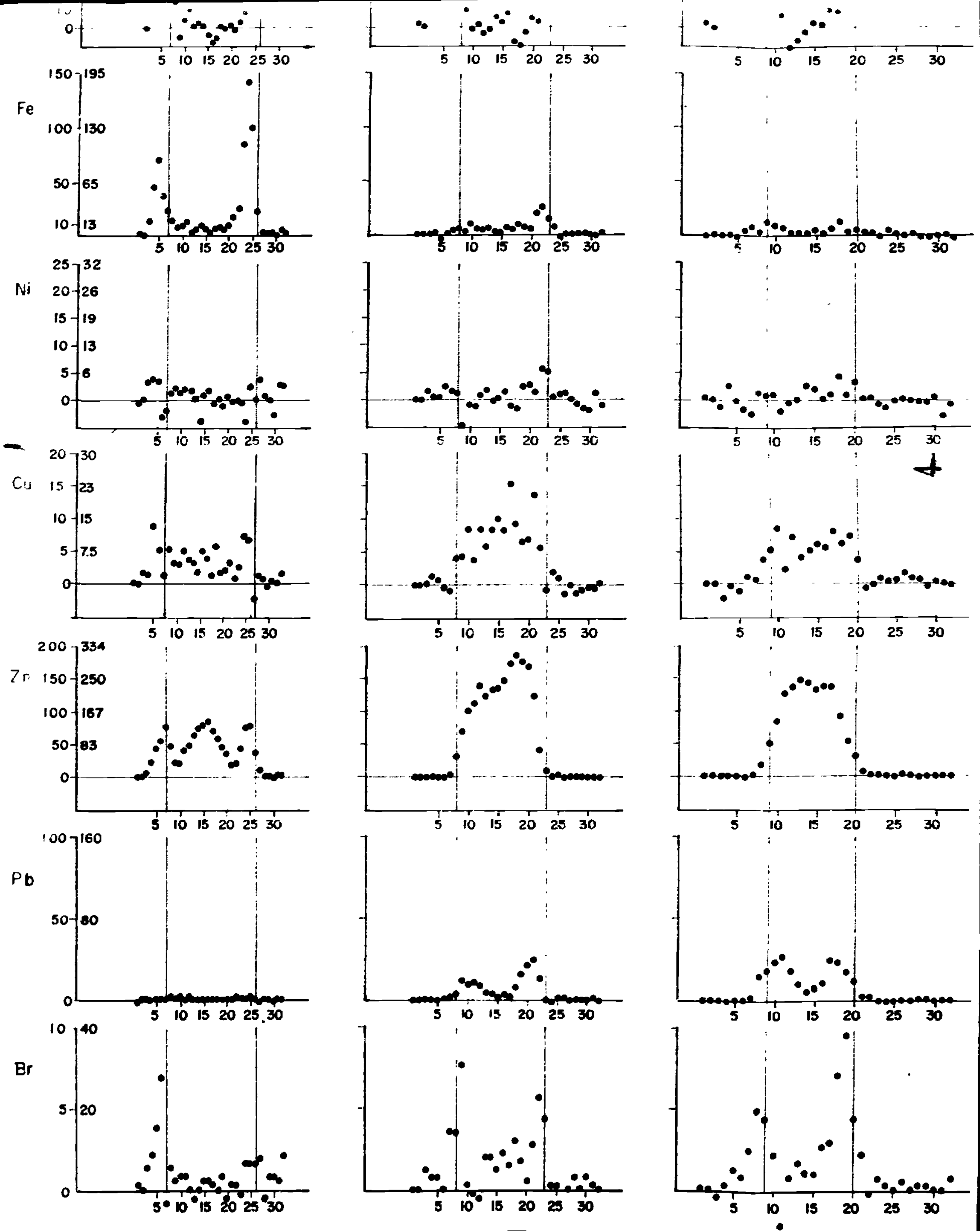






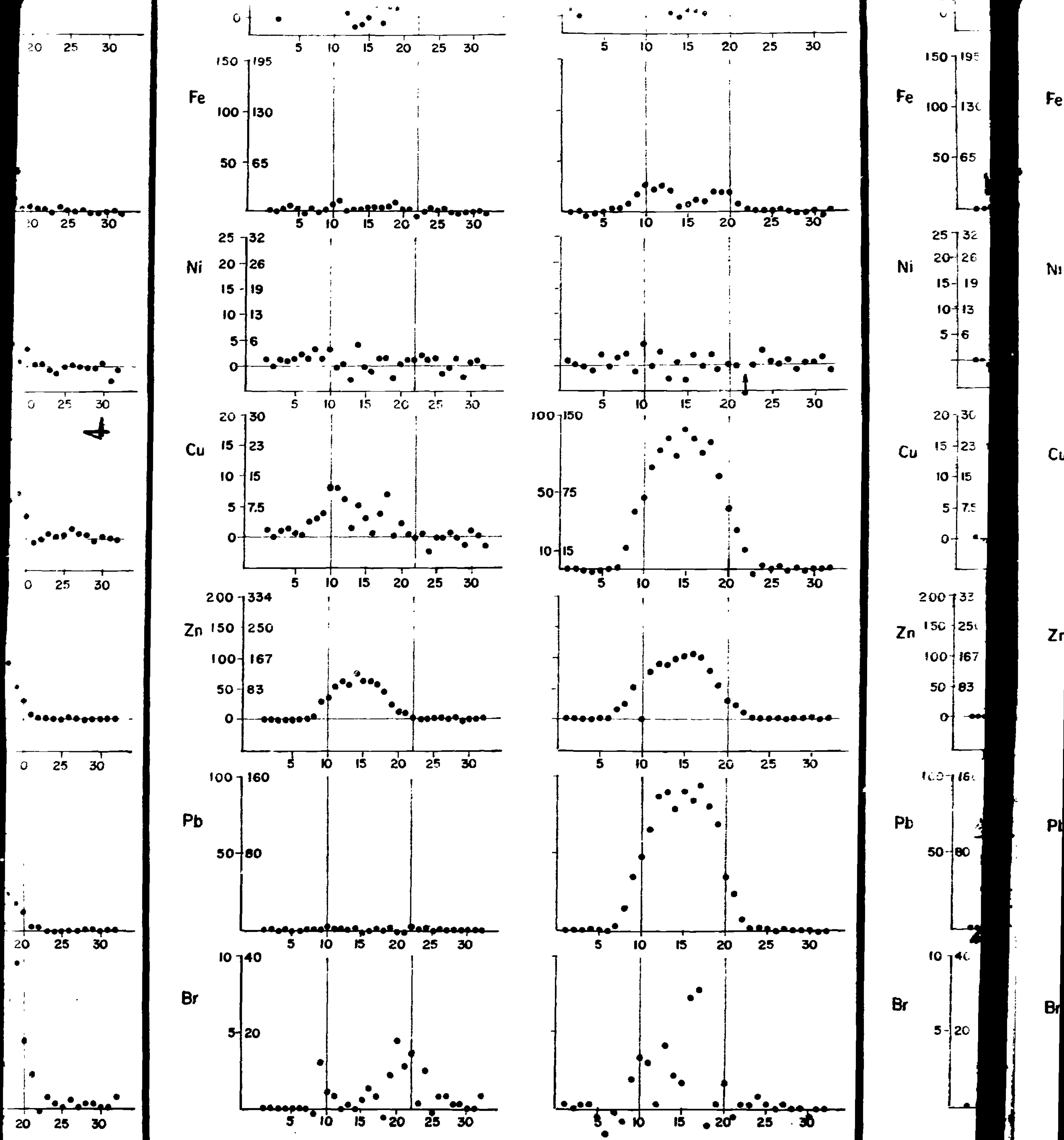
Leg (root) EI
Run 152
Leg (1 cm off root) EII
Run 160
Leg (2cm off root) EIII
Run 155
S
K
Ca
V
Fe
Ni

SECTION 3

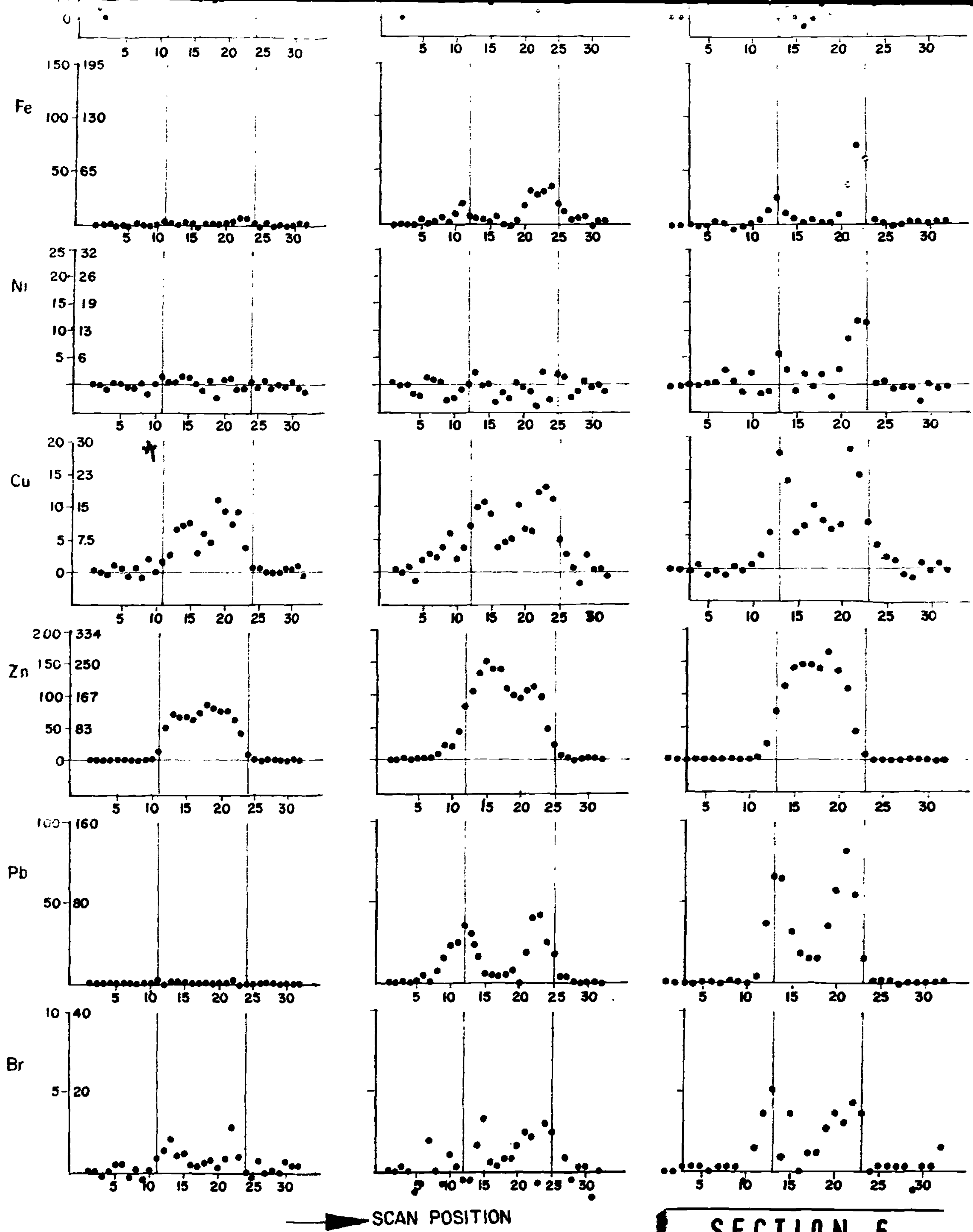


Fe
150 195
100 130
50 65
10 13
Ni
25 32
20 26
15 19
10 13
5 6
0
Cu
20 30
15 23
10 15
5 7.5
0
Zn
200 334
150 250
100 167
50 83
0
Pb
100 160
50 80
0
Br
10 40
5 20
0
5 10 15 20 25 30

SECTION 4



SECTION 5

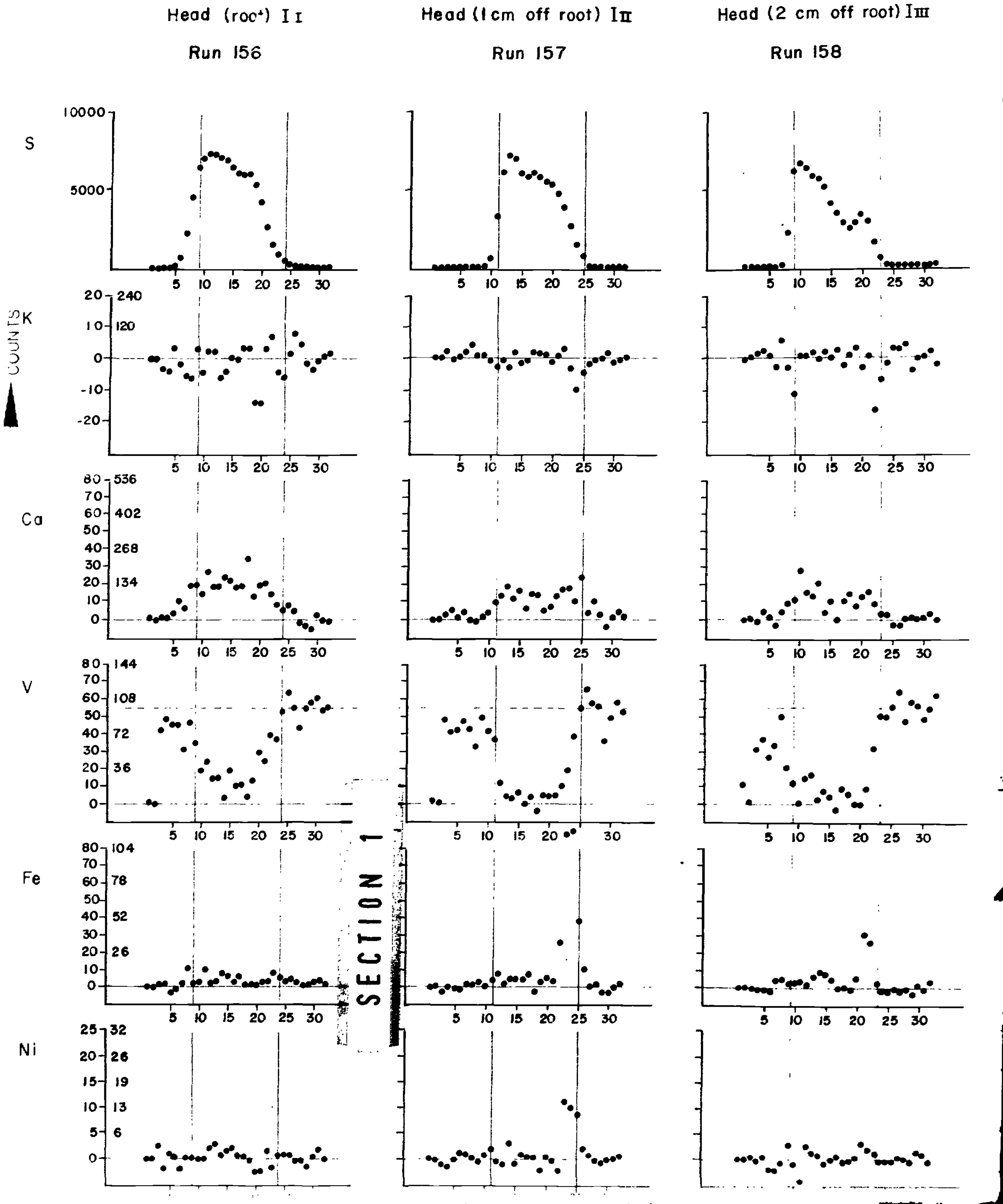

Fe
150 195
100 130
50 65
Ni
25 32
20 26
15 19
10 13
5 6
Cu
20 30
15 23
10 15
5 7.5
0
Zn
200 334
150 250
100 167
50 83
0
Pb
100 160
50 80
Br
10 40
5 20
5 10 15 20 25 30
SCAN POSITION

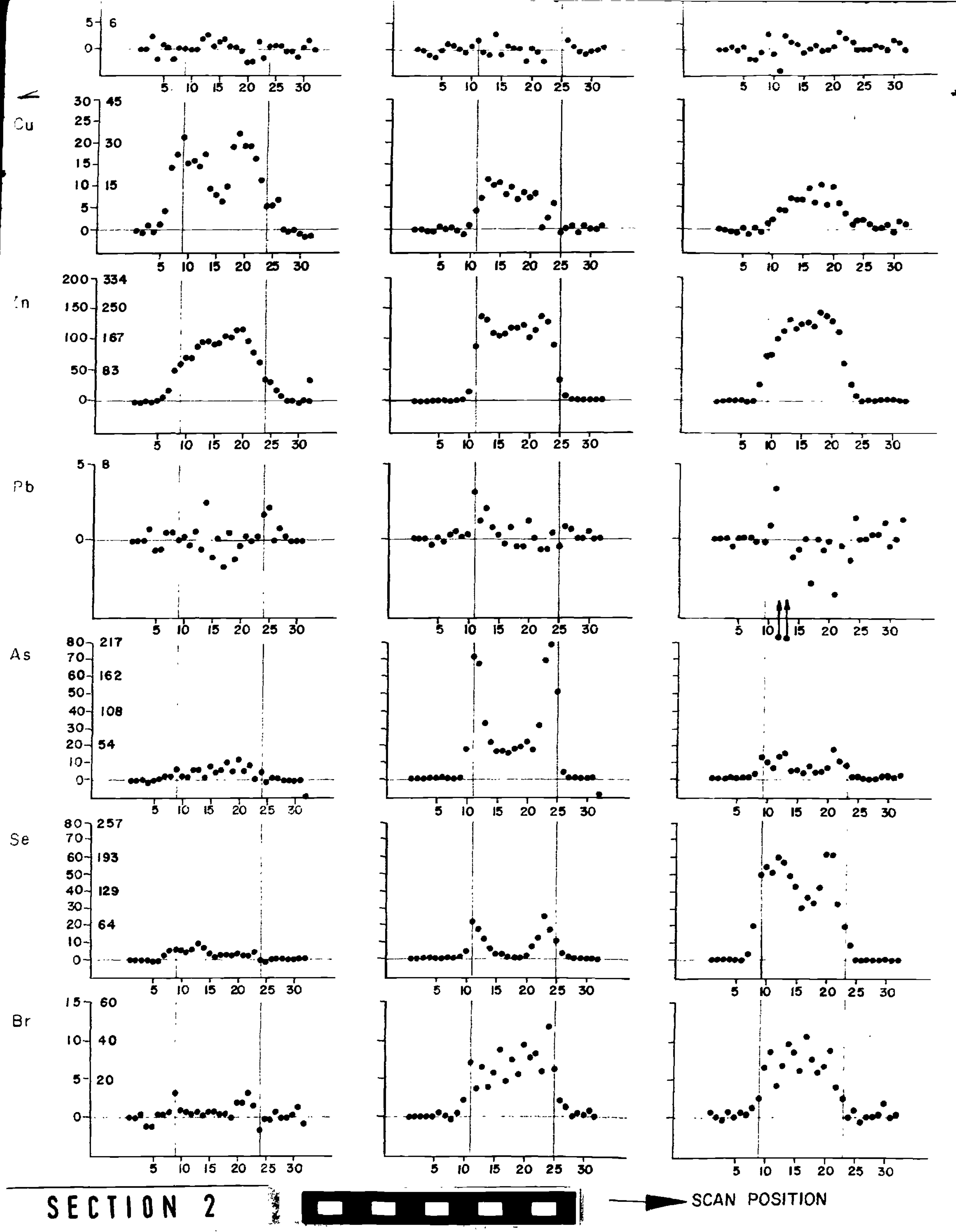
SECTION 6

Appendix III

APPENDIX III

PATIENT of ALEXANDER / LENIHAN





Cu
Zn
Pb
As
Se
Br
30 45
20 30
10 15
200 334
150 250
100 167
50 83
5 8
80 217
60 162
40 108
20 54
80 257
60 193
40 129
20 64
15 60
10 40
5 20
5 10 15 20 25 30
SECTION 2
SCAN POSITION