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*A. K. Perkons,*[1] *Ph.D.; J. A. Velandia,*[1] *Ph.D.; and*
*M. Dienes,*[2] *M.D.*

# Forensic Aspects of Trace Element Variation in the Hair of Isolated Amazonas Indian Tribes

The importance of trace element composition and especially variation in hair in forensic investigations has generated wide interest and controversy during the last decade with the advance of nuclear activation analysis techniques [*1,2*].

Considerable data on the analyses of hair samples of persons from diverse locations in the industrialized parts of the developed world are available, and various conclusions regarding the characterization of individual hair samples have been made [*3–5*]; however, several questions regarding the sources and the variability of trace constituents in the hair of distinct, closed groups of donors exposed to similar diets and environmental conditions, and the probable mechanism of deposition of the trace elements in hair, have still remained open. This work attempts to answer, at least partly, some of these questions by considering the data from an analysis of hair samples collected from donors from two remote areas of the Venezuelan Amazonas area in the tropical jungle of the Orinoco and Ventuari rivers (Fig. 1).

The two groups of donors belong to the sedentary tribes of the extremely primitive Waika Indians of Northern South America. The remoteness of the area, the primitive living conditions, and the very limited and uniform local diets of the Indians serve to avoid any exposure of their biological systems to modern industrial or agricultural contamination in all its forms, both external and metabolic.

Thermal neutron activation analysis was used in the investigation because of its extremely high sensitivity and specificity, thus being the best overall method of analysis providing data on the largest possible number of constituents in the shortest time. Activation analysis also avoids interference from the biological matrices, which are not subject to activation by thermal neutrons, and therefore allow nondestructive instrumental analysis. In addition, the recent advances in high-resolution solid state detector spectrometry has considerably increased the number of elements amenable to accurate instrumental analysis at very low concentration levels in biological media [*6*]. The general theory of activation analysis and its forensic applications has been described in detail previously [*1,6,7*].

## Experimental

Scalp hair samples from eleven native Waika Indian donors of two villages in the Amazonas Territories of Venezuela were collected during an expedition to that area in October 1973. The specimens were cut close to the scalp near the back of the head. Con-

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[1] Instituto Venezolano de Investigaciones Cientificas (IVIC), Táchira, Venezuela.
[2] Universidad Simón Bolívar, San Cristóbal, Táchira, Venezuela.

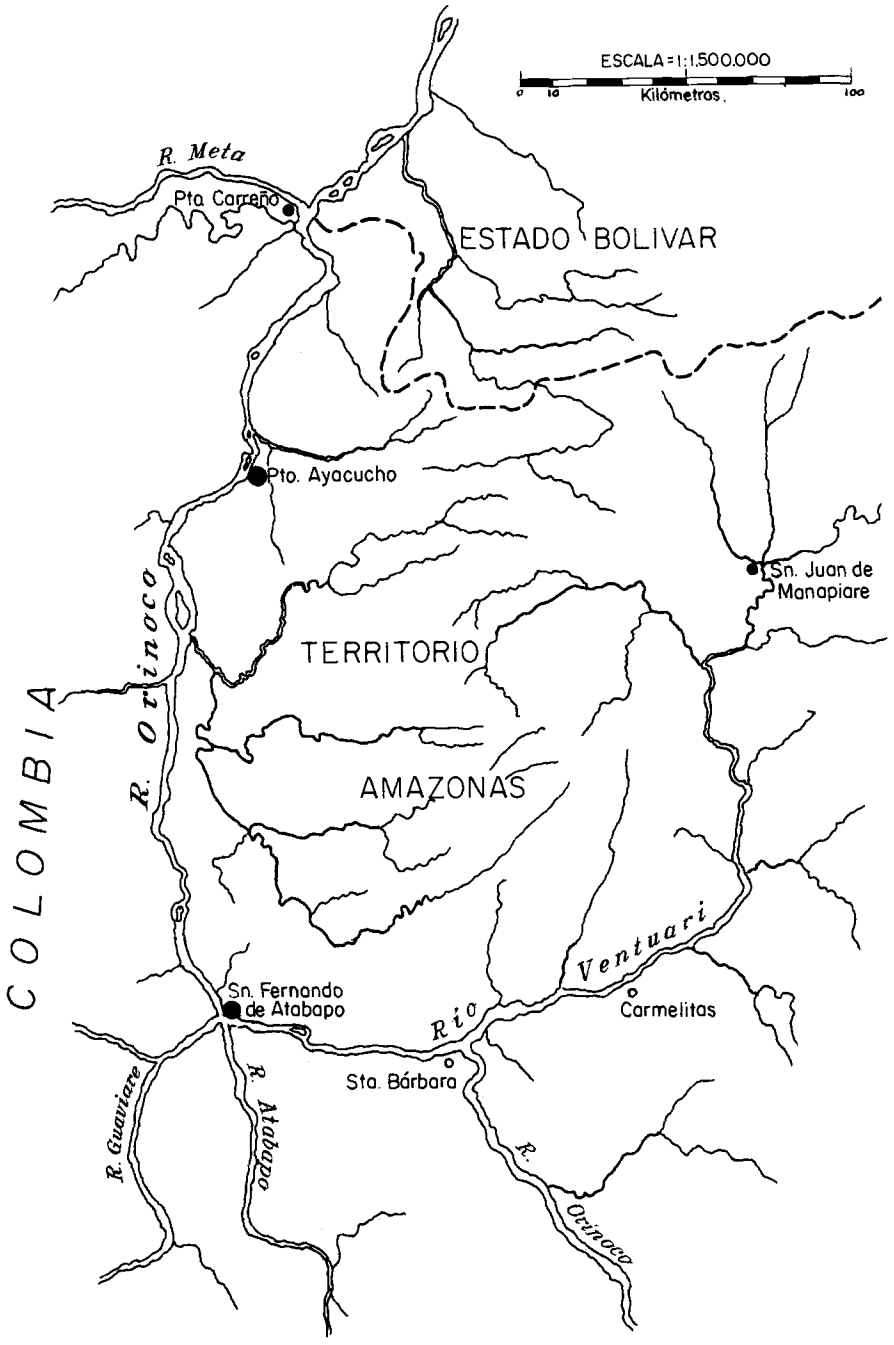


FIG. 1—*Map of the Orinoco-Ventuari area, the Amazonas Territory, Venezuela.*

siderable difficulties were encountered inducing the primitive natives to donate the samples because of their very strong superstitious belief that the hair, being an integral part of their bodies, also contains a part of their souls, and as a consequence the possessor of the hair would exert strong magical power over the donors and control their lives. The hostility, initially quite dangerous, was overcome only with gifts and the active help of the local witch doctors, who in turn demanded generous compensation for their assistance. In spite of all such efforts, only five samples of hair could be obtained from a tribe from a native village near Santa Barbara on the river Orinoco (Samples 1 and 2 are from males and Samples 3 to 5 are from females), and six more from another village near the missionary outpost of Las Carmelitas further up the Ventuari river (Samples 6 and 7 are from males and Samples 8 to 11 are from females) (Fig. 1).

The hair specimens were cleaned of superficial dirt, clay, and grease; weighed; and sealed in plastic vials for short irradiations. The irradiations were carried out in the pneumatic sample transfer system of the RV-1 nuclear reactor at I.V.I.C. (The Venezuelan Institute for Scientific Research) under a thermal neutron flux of $7 \times 10^{11}$ n/cm$^2$·s for 5.0-min periods, followed by 1.0-min transfer time and 1000-s counting time, using an 80-cm$^3$ premium resolution (2.6 eV, full width at half maximum systems resolution for the 1.33 MeV $^{60}$Co peak), Ge(Li) solid-state detector. The gamma spectra were produced with a 4096 channel pulse height analyzer, obtaining both digital and graphic data. Background and blank spectrum subtraction was done for all samples. Several mixed standards were irradiated and counted under the same conditions. Neither pre- nor post-irradiation separations were done, and the hair samples were left intact.

After decay of the induced radioactivity the same samples were weighed again and sealed in smaller quartz ampules for long irradiations, which were carried out in the vertical irradiation tube of the same reactor, under a thermal neutron flux of $1.7 \times 10^{12}$ n/cm$^2$·s, together with mixed standards, for 38 h. The samples were then counted after a decay of 168 to 600 h, using the same analytical system and procedure as before. The counting times were 2 to 24 h. Figures 2 and 3 give representative gamma spectra for the short and long irradiations, respectively. Table 1 lists the nuclear characteristics of all the various isotopes considered in this work.

## Results and Discussion

The quantitative amounts of 30 constituents in the hair samples are presented in Table 2. In addition to these, the presence of seven more components (magnesium, yttrium, niobium, cadmium, europium, hafnium, and tantalum) was detected in the gamma spectra; however, the concentrations could not be quantitated because of interferences or presence of the concentrations below reliable detection limits. Another 18 elements which are occasionally found in biological tissues, including hair, were not found to be present in detectable quantities in this study. These elements are calcium, gallium, zirconium, molybdenum, ruthenium, indium, tin, tellurium, praseodymium, neodymium, gadolinium, terbium, holmium, erbium, thulium, ytterbium, lutetium, and platinum.

It is evident from Table 2 that several constituents are present in these hair samples in much reduced quantities, or are even completely absent in detectable amounts, as compared to a general world population sample [*8*].

Two examples of a comparison of the values obtained in this work with the concentration distribution histograms of previous investigations are given in Figs. 4 and 5 for copper and cesium. Other elements showing reduced concentrations are magnesium, silicon, chlorine, calcium, vanadium, gallium, arsenic, strontium, cadmium, tin, antimony, barium, and samarium. The low concentrations of copper are particularly noteworthy, since that element has previously been closely associated with the color of the hair, black hair containing the highest concentrations, usually between 250 and 400 ppm [*9*].

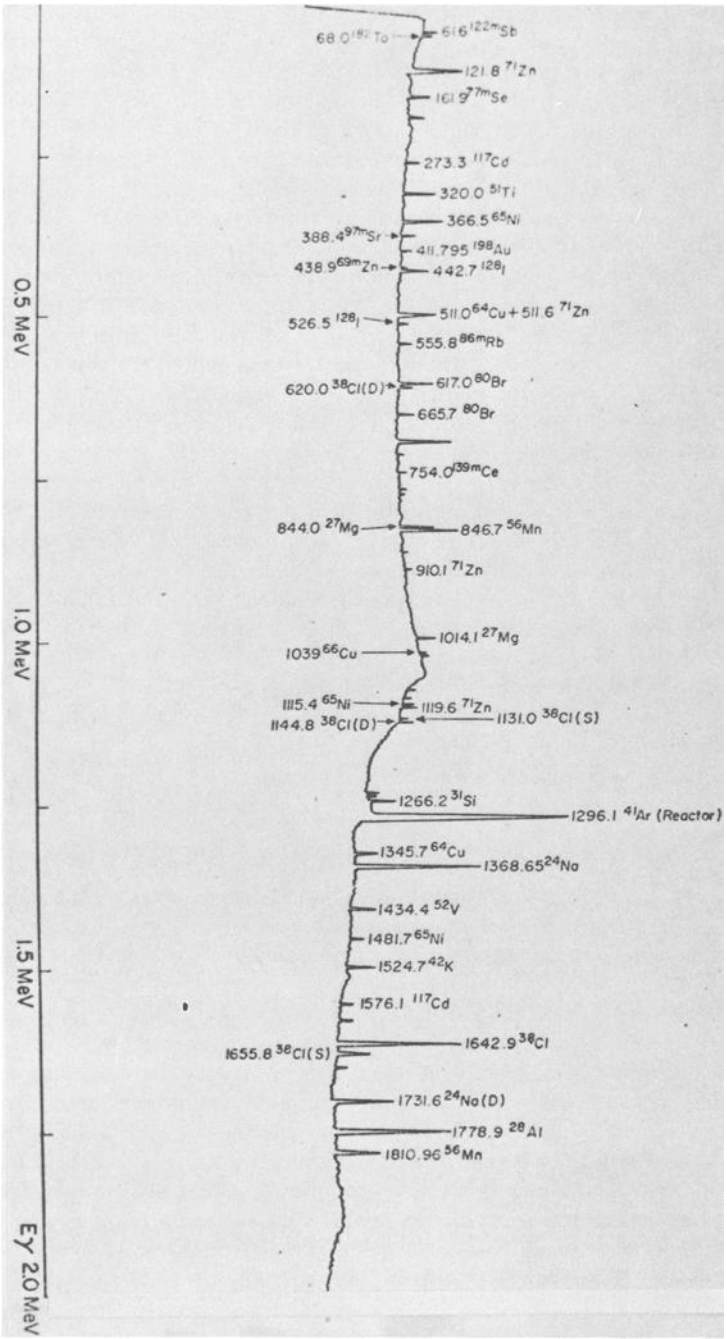


FIG. 2—*Gamma-ray spectrum of short half-life isotopes in hair.*

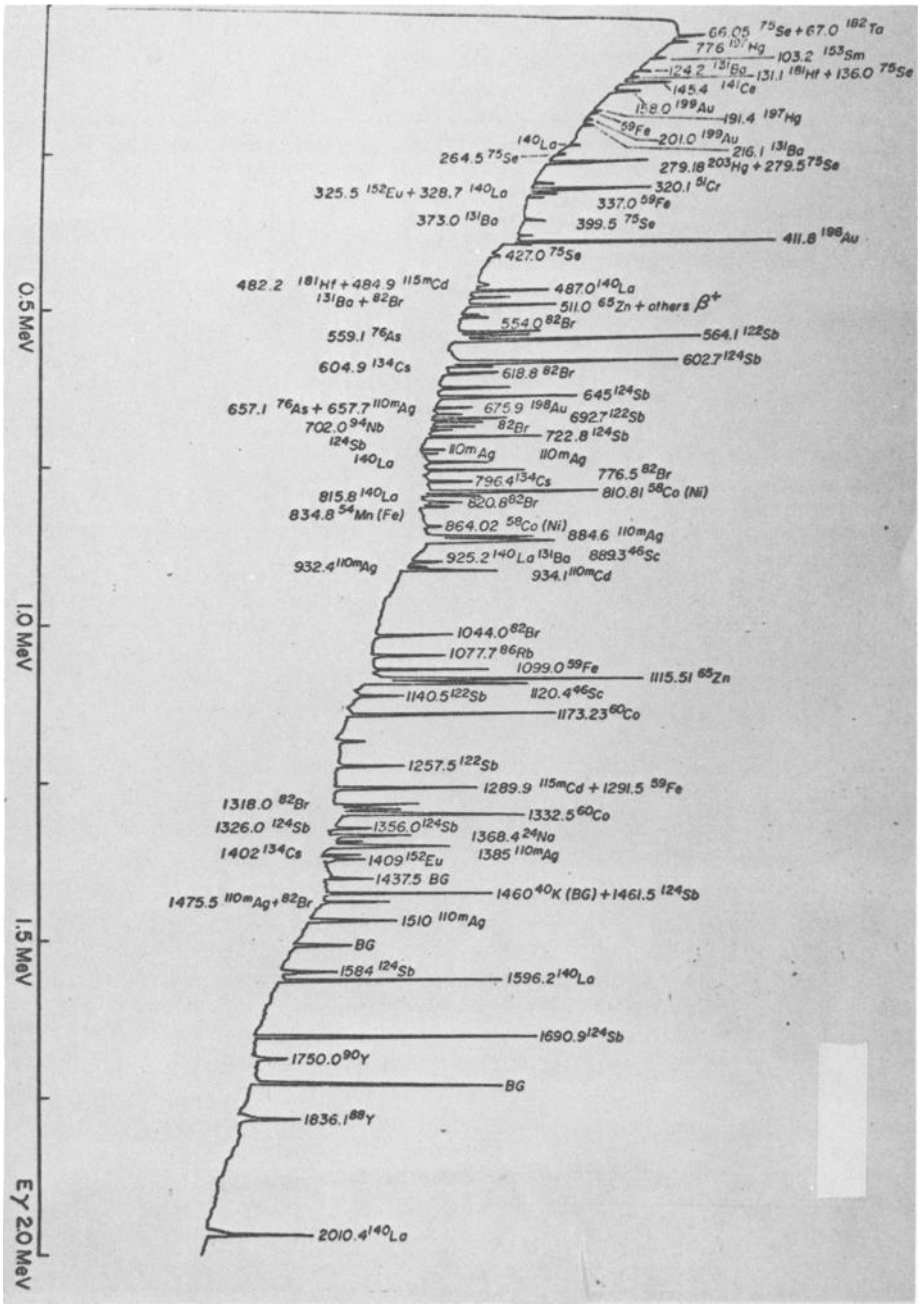


FIG. 3—*Gamma-ray spectrum of long half-life isotopes in hair.*

TABLE 1—*Nuclear characteristics of isotopes found in hair.*

| Element | Nuclear Reaction | Decay Half-Life | | Main Gamma-Energies, keV | | |
|---|---|---|---|---|---|---|
| Na | $^{23}Na(n,\gamma)^{24}Na$ | 15.00 | h | 1368.4 | 2753.9 | ... |
| Mg | $^{26}Mg(n,\gamma)^{27}Mg$ | 9.45 | min | 844.0 | 1014.1 | ... |
| Al | $^{27}Al(n,\gamma)^{28}Al$ | 2.31 | min | 1778.9 | ... | ... |
| Si | $^{38}Si(n,\gamma)^{39}Si$ | 2.62 | h | 1266.2 | ... | ... |
| Cl | $^{37}Cl(n,\gamma)^{38}Cl$ | 37.2 | min | 2167.2 | 1642.9 | ... |
| K | $^{41}K(n,\gamma)^{42}K$ | 14.42 | h | 1524.7 | ... | ... |
| Sc | $^{45}Sc(n,\gamma)^{46}Sc$ | 83.82 | days | 889.3 | 1120.4 | ... |
| Ti | $^{50}Ti(n,\gamma)^{51}Ti$ | 5.79 | min | 320.0 | 605 | 928 |
| V | $^{51}V(n,\gamma)^{52}V$ | 3.76 | min | 1434.4 | ... | ... |
| Cr | $^{50}Cr(n,\gamma)^{51}Cr$ | 27.8 | days | 320.1 | ... | ... |
| Mn | $^{55}Mn(n,\gamma)^{56}Mn$ | 2.582 | h | 846.7 | 1811.0 | ... |
| Fe | $^{54}Fe(n,p)^{54}Mn$ | 313 | days | 834.8 | ... | ... |
| Fe | $^{58}Fe(n,\gamma)^{59}Fe$ | 45 | days | 1099.0 | 1291.5 | ... |
| Co | $^{59}Co(n,\gamma)^{60}Co$ | 5.258 | years | 1173.2 | 1332.5 | ... |
| Ni | $^{64}Ni(n,\gamma)^{65}Ni$ | 2.55 | h | 1481.7 | 366.5 | 1115.4 |
| Ni | $^{58}Ni(n,p)^{58}Co$ | 71.4 | days | 810.7 | ... | ... |
| Cu | $^{63}Cu(n,\gamma)^{64}Cu$ | 12.75 | h | 1345.7 | 511.0 | ($\beta^+$) |
| Cu | $^{65}Cu(n,\gamma)^{66}Cu$ | 5.12 | min | 1039.0 | ... | ... |
| Zn | $^{64}Zn(n,\gamma)^{65}Zn$ | 243.7 | days | 1115.5 | ... | ... |
| Zn | $^{68}Zn(n,\gamma)^{69\,m}Zn$ | 13.7 | h | 438.9 | ... | ... |
| Zn | $^{70}Zn(n,\gamma)^{71}Zn$ | 2.2 | min | 511.6 | 121.8 | 910.1 |
| As | $^{75}As(n,\gamma)^{76}As$ | 26.4 | h | 559.1 | 657.1 | ... |
| Se | $^{74}Se(n,\gamma)^{75}Se$ | 120.4 | days | 136.0 | 264.7 | 279.5 |
| Se | $^{76}Se(n,\gamma)^{77\,m}Se$ | 17.5 | s | 161.9 | ... | ... |
| Br | $^{79}Br(n,\gamma)^{80}Br$ | 17.6 | min | 618.0 | 666.0 | ... |
| Br | $^{81}Br(n,\gamma)^{82}Br$ | 35.4 | h | 554.0 | 776.5 | 619.1 |
| Rb | $^{85}Rb(n,\gamma)^{86\,m}Rb$ | 1.0 | min | 555.8 | ... | ... |
| Rb | $^{85}Rb(n,\gamma)^{86}Rb$ | 18.66 | days | 1077.7 | ... | ... |
| Sr | $^{86}Sr(n,\gamma)^{87\,m}Sr$ | 2.83 | h | 388.5 | ... | ... |
| Y | $^{89}Y(n,\gamma)^{90}Y$ | 64.0 | h | 1750.0 | ... | ... |
| Nb | $^{93}Nb(n,\gamma)^{94}Nb$ | 20 000 | years | 702.0 | ... | ... |
| Ag | $^{109}Ag(n,\gamma)^{110\,m}Ag$ | 253 | days | 657.7 | 884.6 | 932.4 |
| Cd | $^{114}Cd(n,\gamma)^{115\,m}Cd$ | 44.1 | days | 934.1 | 484.9 | 1289.9 |
| Sb | $^{121}Sb(n,\gamma)^{122\,m}Sb$ | 4.2 | min | 61.0 | 75.0 | ... |
| Sb | $^{121}Sb(n,\gamma)^{122}Sb$ | 2.74 | days | 564.1 | 692.7 | 1140.6 |
| Sb | $^{123}Sb(n,\gamma)^{124}Sb$ | 60.2 | days | 602.7 | 722.8 | 1690.9 |
| I | $^{127}I(n,\gamma)^{128}I$ | 25.0 | min | 443.0 | 526.4 | ... |
| Cs | $^{133}Cs(n,\gamma)^{134}Cs$ | 2.06 | years | 604.9 | 570.1 | 796.4 |
| Ba | $^{130}Ba(n,\gamma)^{131}Ba$ | 11.5 | days | 124.2 | 216.1 | 375.1 |
| La | $^{139}La(n,\gamma)^{140}La$ | 40.23 | h | 1596.0 | 328.7 | 815.8 |
| Ce | $^{140}Ce(n,\gamma)^{141}Ce$ | 32.53 | days | 145.5 | ... | ... |
| Sm | $^{152}Sm(n,\gamma)^{153}Sm$ | 46.8 | h | 103.2 | 69.7 | ... |
| Eu | $^{151}Eu(n,\gamma)^{152}Eu$ | 14 | years | 121.8 | 344.2 | 1407.8 |
| Hf | $^{180}Hf(n,\gamma)^{181}Hf$ | 42.4 | days | 482.2 | 133.1 | 345.9 |
| Ta | $^{181}Ta(n,\gamma)^{182}Ta$ | 115.1 | days | 68.0 | 1122.0 | 1222.0 |
| Au | $^{197}Au(n,\gamma)^{198}Au$ | 2.696 | days | 411.8 | 675.9 | ... |
| Au | $^{197}Au(2n,\gamma)^{199}Au$ | 3.15 | days | 158.0 | 201.0 | ... |
| Hg | $^{196}Hg(n,\gamma)^{197}Hg$ | 64.1 | h | 77.6 | 191.4 | ... |
| Hg | $^{202}Hg(n,\gamma)^{203}Hg$ | 46.6 | days | 279.2 | ... | ... |

TABLE 2—*Elemental concentrations (ppm).*

| Element | Sample 1, 8.77 mg | Sample 2, 11.12 mg | Sample 3, 10.00 mg | Sample 4, 3.74 mg | Sample 5, 4.74 mg | Sample 6, 12.45 mg | Sample 7, 12.45 mg | Sample 8, 18.08 mg | Sample 9, 10.59 mg | Sample 10, 12.67 mg | Sample 11, 8.48 m | Precision | | | Values from Previous Analyses | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | Mean | ±σ | % | Range | Mean |
| Na | 1719 | 1090 | 1424 | 950 | 1506 | 2931 | 1937 | 1145 | 488 | 2562 | 1440 | 1562 | 30 | 1 | 200 to 5600 | 1600 |
| Al | 28.9 | 31.4 | 21.6 | 35.3 | 30.8 | 38.2 | 27.3 | 33.5 | 29.4 | 32.7 | 27.5 | 30.6 | 2.5 | 8 | ... | ... |
| Si | 0.02 | 0.04 | 0.03 | 0.01 | 0.01 | 0.02 | 0.03 | 0.03 | 0.01 | 0.04 | 0.03 | 0.025 | 0.005 | 20 | ... | ... |
| Cl | 17.6 | 22.9 | 21.3 | 22.6 | 20.3 | 26.8 | 22.2 | 20.1 | 18.3 | 25.2 | 22.0 | 21.8 | 1.4 | 6.5 | 15 to 460 | 150 |
| K | 2095 | 2160 | 1995 | 2195 | 2340 | 1895 | 2100 | 2165 | 2370 | 2245 | 2140 | 2155 | 75 | 3.5 | 200 to 6700 | 1800 |
| Sc | 0.0068 | 0.0133 | 0.0158 | 0.0121 | 0.0142 | 0.0178 | 0.0094 | 0.0137 | 0.0173 | 0.0109 | 0.0126 | 0.0131 | 0.0005 | 4 | N.D. to 0.0250 | 0.0070 |
| Ti | 26.2 | 23.2 | 27.9 | 30.4 | 21.1 | 33.9 | 23.8 | 29.3 | 27.0 | 23.2 | 27.6 | 26.7 | 2.5 | 9 | ... | ... |
| V | 0.52 | 0.14 | N.D. | 0.07 | 0.21 | 0.34 | 0.03 | 0.75 | 0.14 | N.D. | 0.32 | 0.23 | 0.005 | 2 | N.D. to 2.00 | 0.60 |
| Cr | 7.9 | 8.2 | 8.9 | 7.7 | 7.7 | 8.8 | 8.3 | 9.6 | 7.4 | 8.3 | 8.5 | 8.3 | 0.5 | 6 | N.D. to 21.5 | 3.5 |
| Mn | 6.820 | 2.225 | 6.380 | 1.520 | 5.460 | 3.235 | 2.150 | 8.235 | 2.455 | 3.550 | 1.230 | 3.935 | 0.005 | <1 | N.D. to 28.0 | 6.0 |
| Fe | 65 | 79 | 53 | 65 | 87 | 58 | 56 | 74 | 66 | 67 | 46 | 65 | 10 | 15.5 | N.D. to 230 | 35 |
| Co | 2.30 | 1.26 | 0.53 | 1.52 | 1.95 | 1.51 | 1.21 | 2.83 | 1.82 | 2.32 | 1.42 | 1.70 | 0.10 | 6 | N.D. to 8.00 | 0.55 |
| Ni | 48 | 56 | 64 | 43 | 62 | 54 | 59 | 71 | 47 | 53 | 68 | 57 | 5 | 9 | N.D. to 240 | 4.5 |
| Cu | 11.0 | 6.3 | 102.0 | 12.1 | 9.4 | 2.5 | 13.5 | 5.2 | 19.4 | 8.8 | 9.8 | 18.2 | 2.0 | 11 | N.D. to 490 | 120 |
| Zn | 330 | 260 | 380 | 285 | 155 | 465 | 295 | 330 | 290 | 200 | 395 | 308 | 25 | 8 | N.D. to 3200 | 620 |
| As | N.D. | 0.20 | N.D. | N.D. | N.D. | 0.70 | 1.15 | 0.65 | 0.90 | 0.95 | 0.75 | 0.50 | 0.10 | 20 | N.D. to 11.5 | 1.75 |
| Se | 5.15 | 4.80 | 4.35 | 5.45 | 4.75 | 2.60 | 3.15 | 2.15 | 2.95 | 2.35 | 2.80 | 3.68 | 0.80 | 12 | N.D. to 7.5 | 1.80 |
| Br | 31.6 | 29.4 | 34.5 | 28.9 | 30.9 | 48.0 | 32.8 | 27.0 | 29.1 | 32.8 | 25.6 | 31.9 | 1.5 | 4.5 | N.D. to 1500 | 55.0 |
| Rb | 0.80 | 1.10 | 0.40 | 2.60 | 0.60 | 0.20 | 3.40 | 2.30 | 1.30 | 0.60 | 1.70 | 1.35 | 0.20 | 15 | N.D. to 14.00 | 1.50 |
| Sr | 0.02 | 0.01 | N.D. | 0.04 | 0.02 | 0.02 | 0.04 | N.D. | 0.03 | N.D. | 0.02 | 0.02 | 0.02 | 100 | N.D. to 0.27 | 0.04 |
| Ag | 0.60 | 1.75 | 0.35 | 1.20 | 1.85 | 0.20 | 0.55 | 1.05 | 0.80 | 0.25 | 0.95 | 0.87 | 0.15 | 17 | N.D. to 15.0 | 0.75 |
| Sb | N.D. | 1.70 | 3.10 | N.D. | N.D. | 2.55 | 0.40 | 1.85 | 2.15 | N.D. | 1.80 | 1.25 | 0.10 | 8 | N.D. to 45.0 | 10.0 |
| I | 12.7 | 13.2 | 14.7 | 11.2 | 13.8 | 12.6 | 15.3 | 14.0 | 11.8 | 12.7 | 15.8 | 13.4 | 1.2 | 9 | N.D. to 80.0 | 12.0 |
| Cs | 0.27 | 1.18 | 0.21 | 0.54 | 0.40 | N.D. | N.D. | 0.75 | 0.14 | 0.49 | 0.10 | 0.38 | 0.20 | 53 | N.D. to 4.80 | 1.20 |
| Ba | 0.4 | 0.8 | 0.3 | 0.2 | 0.3 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.2 | 0.05 | 25 | N.D. to 112.8 | 5.0 |
| La | 0.72 | 0.67 | 0.45 | 0.22 | 0.89 | 0.57 | 0.86 | 0.13 | 1.11 | 0.31 | 0.48 | 0.58 | 0.05 | 8.5 | N.D. to 2.70 | 0.32 |
| Ce | 0.31 | 0.19 | 0.07 | 0.41 | 0.02 | N.D. | 0.24 | 0.15 | 0.08 | 0.16 | 0.11 | 0.16 | 0.10 | 63 | ... | ... |
| Sm | N.D. | N.D. | 0.010 | 0.010 | 0.015 | 0.020 | 0.010 | N.D. | N.D. | 0.005 | N.D. | 0.010 | 0.0025 | 25 | N.D. to 0.860 | 0.020 |
| Au | 1.995 | 1.780 | 1.500 | 2.010 | 2.255 | 2.130 | 2.895 | 1.725 | 2.620 | 1.805 | 2.180 | 2.080 | 0.0005 | <1 | 0.005 to 6.010 | 1.350 |
| Hg | 2.70 | 2.75 | 3.25 | 2.20 | 3.55 | 4.15 | 1.70 | 2.90 | 2.45 | 3.70 | 3.45 | 2.98 | 0.25 | 8.5 | N.D. to 6.80 | 1.55 |

[a] N.D. = not detected.

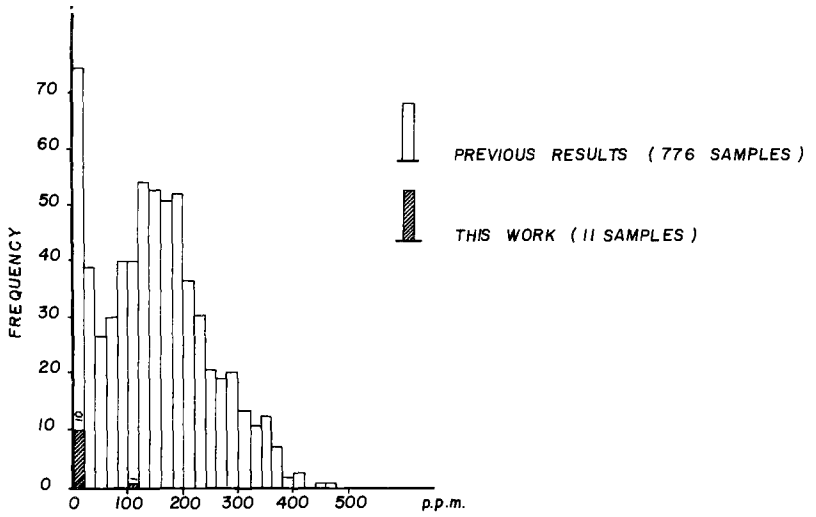


FIG. 4—*Copper concentrations in hair.*

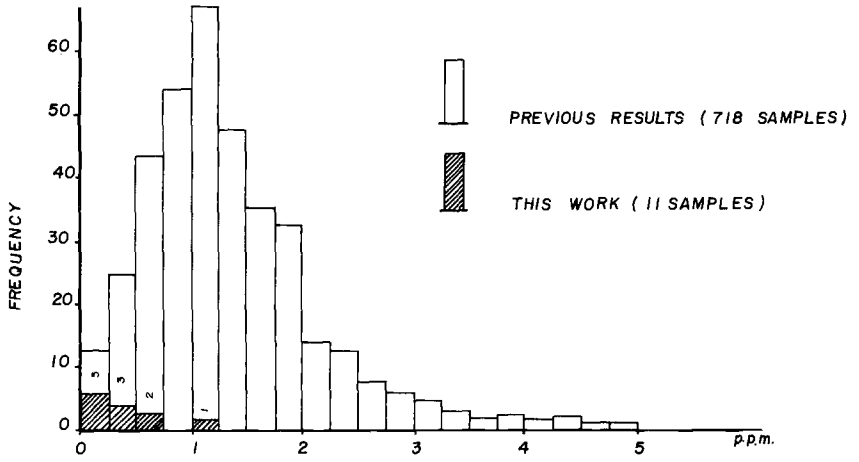


FIG. 5—*Cesium concentrations in hair.*

In this investigation, although all the hair samples were black, only one specimen contained a somewhat elevated amount of copper (102.0 ppm), the others having concentrations of less than 20 ppm. The conspicuous absence of detectable amounts of calcium in the hair reflects a well-known condition of general calcium deficiency in the biosphere of the Orinoco—Ventuari area.[3] Some high-toxicity industrial pollutants, such as arsenic and cadmium, are also low. The rather high titanium content may be due to regionally high geological abundance of $TiO_2$.

A very important observation from the forensic point of view concerns the concentration ranges of most elements in all the hair samples. With the exception of only five constituents (sodium, manganese, cobalt, rubidium, and lanthanum), the concentration ranges are very narrow as compared to the generally very wide distribution found in

[3] Private communication, J. Racenis, Entymology Dept., Universidad Central de Venezuela.

previous work [*4,8,9*]. An example of this is demonstrated in Fig. 6 for gold. This clustering of the concentrations tends to indicate that a large proportion of the contaminants in hair of persons exposed to a more varied industrial environment are incorporated in the hair externally, and any metabolic deposition may occur much more uniformly.

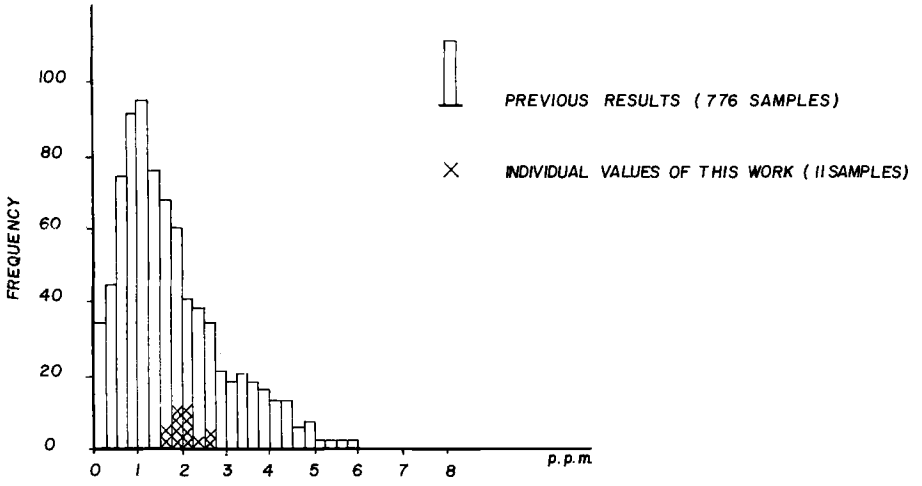


FIG. 6—*Gold concentrations in hair.*

More important, it indicates that for special, closed population groups the concentrations of the constituents in hair can be much closer than the general population spread and, therefore, the individualization of members of such groups exposed to similar diets and environments is indeed much more difficult than previously supposed [*5,8*]. In fact, the probability of encountering two individuals with similar trace element concentration patterns for several elements, within the limits of standard deviations and the inherent variability in one donor, approaches 1:1 within such groups. Obvious and, from the forensic standpoint, very important groups of this kind could be a specific prison population, or other institutional populations, including inmates recently released.

A curious occurrence in the data of Table 2 is the presence of comparatively high amounts of chromium, nickel, selenium, gold (see also Fig. 6), and mercury—elements usually associated with industrial contamination. The only explanation, especially in view of the very narrow concentration ranges in all the samples, seems to be a high concentration of these elements in the daily diets, that is, in the local biosphere. It is tempting to speculate on the presence of significant geological deposits of the ores of these elements in the unexplored region, leading to the use of analysis of hair as a prospecting tool.

A final observation indicates a uniform ingestion of trace elements with similar diets, evident from the close agreement between most of the concentration values between the two groups of donors. Only three of the elements, namely arsenic, selenium, and barium, show distinct differences in concentrations between the two groups, indicating possible differences in dietary ingestion of these elements in the two villages. Of course, possible inherited metabolic factors in this regard cannot be discounted, as the different tribes are genetically somewhat differentiated by separate evolution, with very little intermixing.[3,4]

Some directions of further investigation, indicated by this work, should include the analysis of larger samples of isolated or primitive communities, an analysis of the com-

[4] Private communication, E. Foldats, Botany Dept., Universidad Central de Venezuela.

ponents of their respective diets and biospheres, and the analysis of hair samples from closed institutional groups.

The conclusion that isolated population groups can exhibit a high degree of similarity in their hair composition is in agreement with previous studies on families and twins [7], where it was shown that the trace element similarities decreased with increased separation and variation of the diets and environments of the group members. However, the earlier belief that even members of such groups can be reliably differentiated by their hair composition must be modified in the light of the data from this work.

**Summary**

Thermal neutron activation analysis and instrumental gamma-ray spectrometry were used to analyze the elemental constituents in the head hair from sedentary Indian populations in the Venezuelan Amazonas region. Concentration values for 30 elements were determined quantitatively, and the presence of 7 others was detected qualitatively.

The remoteness of the area and the primitive ecological conditions of the local population prevents the exposure of their biological systems to industrial and agricultural contamination, either external or metabolic. These conditions are reflected in a marked decrease of the concentration ranges of the trace elements, and a significant reduction or even the total absence of some components. The results demonstrate that closed groups of individuals exposed to similar dietary and environmental conditions exhibit closely similar trace element patterns in their hair and, consequently, in other biological tissue. This fact severely limits the use of trace element patterns in hair for forensic comparisons. The results also indicate that a large part of the constituents found in hair is probably deposited externally from ambient contamination and that any metabolic deposition occurs much more uniformly and probably in lower concentrations.

Tables of analytical results in parts per million are presented, together with representative gamma-ray spectra of the hair. Comparison with earlier data in the literature is also shown.

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A. K. Perkons, Ph.D.
U. N. E. T.
Apartado Postal 436
San Cristóbal, Edo. Táchira
Venezuela