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The Variation of Trace Element Concentrations in Single Human Head Hairs

Hair from the human body is frequently encountered in the examination of crime-scene physical evidence. Study of metallic components by neutron activation analysis (NAA) and application of the results of such studies in forensic work, have been made difficult by the complexity of the hair system and its attendant surface contamination. As was noted in 1967 [1], "virtually everyone working with hair by this method [NAA] uses a different type of sampling, and a different method of cleaning the hair, and nobody yet really knows enough about the basic chemistry, morphology and behaviour of the hair shaft to be able to assess reliably the significance of the results." The literature [2,3] contains both optimistic and pessimistic prognoses of the possibility of establishing whether or not a hair came from the head of a given individual.

This problem of "characterizing" hair has been analyzed according to a statistical model by Parker [4,5]. He showed that, for successful characterization, three kinds of quantity must be known:

(a) the variation of the average trace element concentrations in hair throughout the population,

(b) the variation of the trace element concentrations among the hairs on individual human heads (both at a given time and as a function of time), and

(c) the analytical error.

As regards the first of these, three substantial surveys of head hair from samples of the population have been conducted [6-10]. Although each used a different procedure for cleaning the hair and there was some variation in the technique used to obtain hair samples, the results may indicate sufficiently accurately for characterization purposes the distribution of concentrations of a number of trace elements in the general population—at least for samples weighing several milligrams or more, if not for single hairs.

Much less is known about the variation of trace element concentrations among and along individual hairs from a given individual. Measurements on single hairs are admittedly difficult in view of the tiny quantities of material to be determined. On the other hand, it is single hairs that most often are encountered in the investigation of a crime, and any practical method of hair characterization must be capable of dealing with single hairs,

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rather than hair bunches. Clearly, it then becomes important to establish the extent of variability in trace elements of the hairs on individual human heads. If this is "large" [3], even as large as the variability among the human population as a whole, then identification of an individual by analysis of just one hair becomes impossible.

Early studies of the variability of the hairs on a single head were conducted partly with hair bunches or strands [10] rather than with single hairs [11], and often by comparisons of spectra obtained with limited-resolution NaI(Tl) γ -detectors. Initial conclusions were that the variability of the hairs of a single indivudual was "slight" [12,13]; later studies [8,14,15] showed that it was substantial.

Parker's third concern, the analytical error, should include effects of changes in the trace element content of hair caused by cleaning [16,17,18]. From a forensic point of view, separating "extraneous" trace elements from those actually incorporated into the hair structure may not be relevant or desirable, because hair contamination may be a valuable identifying characteristic. On the other hand, a hair, which has been contaminated in a way different from those with which it is to be compared should, perhaps, be cleaned first; also cleaning may conceivably reduce hair to hair variations for a single individual and hence facilitate identification.

Another concern involves possible differences in concentrations between hairs in the anagen (active) and telogen (resting) phases of the growth cycle [11].

This paper describes work directed toward contributing to the knowledge of trace element concentration variations in single hairs from a given individual. It has profited from the high energy resolution of lithium-drifted germanium (Ge(Li)) γ -detectors which have become available since much of the early work in this field was performed. In particular it is directed to measurement of the concentration of a number of trace elements in single hairs as a function of location on the scalp, distance along the hair from the scalp, hair growth phase, and hair pretreatment, all as a prelude to hair comparison experiments.

Experimental Techniques

Two series of experiments were performed. The first (series A) employed samples containing many individual human head hairs and weighing several hundreds of milligrams; this was directed toward the exploration of the analytical method and in particular the establishment of the reproducibility of the concentration results. The second (series B) employed samples consisting of single segments of individual head hairs with lengths of roughly 10 cm, and was directed toward the measurement of concentration variations.

Hair Sampling, Washing and Encapsulation Techniques

For experiments in series A, two locks of hair (weighing 800 and 300 mg, respectively) were cut from the head of male subject A. This hair was not subjected to any washing or cleaning procedure before encapsulation. For the larger sample, encapsulation was in a quartz ampule cleaned prior to insertion of the hair by treatment with boiling concentrated HNO₃ and two rinses with boiling distilled, deionized water. The ampule was not sealed during neutron irradiation in order to avoid possible pressure build-up and shattering. The smaller sample was wrapped in 99.999 percent pure aluminum foil.

For experiments in series B, individual hairs were plucked from various sites on the head of female subject B, of which the locations were noted. The subject had never used hair dyes or the equivalent. She had however employed shampoos and cream rinses, particularly on the hair beyond 20 to 30 cm from the scalp. Touching of the hair with bare fingers during plucking was avoided. Disposable plastic gloves, teflon-coated forceps, and envelopes folded from fresh filter paper were employed.

For single hair experiments, the root and the first 1-cm portion of each hair nearest the scalp were cut off (by a clean razor blade) to avoid gross contamination with scalp material; for the second series of these experiments, the hairs were sorted according to whether they were in the anagen or telogen phase of the hair growth cycle. This was achieved by microscopic examination of the cut-off root segments by five individuals, working independently [19]. A hair was taken to be positively identified as to growth phase when four or five observers were in agreement. The remainder of the hairs were then cut (by a clean razor blade) into segments roughly 10 cm long, and weighed. Weights were on the order of 600 μ g, known to within 20 μ g, and are shown in Tables 1, 2, and 3.

Two washing procedures were investigated in separate experiments. In the initial single hair experiments, hair segments were boiled with distilled, deionized water for 3 min, and then rinsed with a portion of cold distilled, deionized water for 10 s, and allowed to dry by evaporation at room temperature.

In the later more extensive experiments, the hair segments were washed [11] successively with portions of diethyl ether (Fisher anhydrous), acetone (Fisher spectroscopy grade), distilled, deionized water, acetone, ether, acetone, water, acetone, and finally ether. Washing time was 60 s in each solvent, and the hairs were dried at room temperature for several hours.

The segments were then individually encapsulated in quartz capillary tubes of 1-mm internal diameter and roughly 3 cm in length, previously cleaned by treatment with boiling, concentrated nitric acid and distilled, deionized water. Insertion of the hair of a given 10-cm segment into a capillary required prior cutting into 2 to 3-cm lengths. The sealed tubes were found to successfully resist the internal pressures generated in the bombardment.

Quartz capillaries were also employed for encapsulation of known quantities of up to 20 elements expected to be encountered in a particular hair analysis. The quantities were chosen according to the respective neutron-capture cross sections, and were obtained by

Hair Identifi- cation Number	Location and distance from scalp	Segment weight (µg)	Preparation	Zn	Se	Au
1	Crown 1-11 cm	750	None	237 ppm	25 ppm	5 ppb
1	11–21 cm	720		216	43	11
1	21-31 cm	750		212	57	19
1	31–41 cm	790		179	45	26
1	41–51 cm	770		224	68	51
2	Crown 1-11 cm	540	Washed	314	21	11
2	11–21 cm	530		353	52	16
2	21–31 cm	620		297	52	23
2	31–41 cm	630		276	51	25
2	41–51 cm	590		348	75	46
3	Temple 1–11 cm	620	None	285	8	19
3	11–21 cm	540	Washed	262	31	47
4	Nape 1–11 cm	510	None	276	23	69
4	11–21 cm	630	Washed	217	52	141
5	Above 1–11 cm	490	None	281	19	9
5	right ear 11–21 cm	480	Washed	253	42	21
6	Above 1–11 cm left ear	640	None	261	11	8

TABLE 1—Trace element concentrations in 10-cm segments of single hairs.

TABLE 2—Trace element content of hairs, in the anagen phase, taken from various scalp locations (segments between 1 and 11 cm from root).

	TABLE 2	-Trace elei	nent conten	t of hairs, in the	anagen pha	se, taken frc	om various su	calp locations (segments bet	ween I and	11 cm from	root).
Hair lenti- ation umber	Location on head	Prepara- tion	Segment weight, μg	Cr, ppm	Fe, ppm	Co, ppb	Zn, ppm	Se, ppm	Ag, ppb	Sb, ppb	Au, ppb	Hg, ppm
t t	Crown	Washed	570	1.58 ± 0.04	19 ± 1	32 ± 3	197 ± 5	4.0 ± 0.3	<70	<10	10 ± 1	1.5 ± 0.1
7			430	0.54 ± 0.11	<11	42 ± 10	197 ± 5	12 ± 1	06>	<10	19 ± 2	1.55 ± 0.06
÷			460	0.58 ± 0.04	14	38 ± 8	201 ± 4	5.4 ± 0.6	240 ± 10	111 ± 9	12 ± 1	1.48 ± 0.08
4		None	550	0.75 ± 0.06	14	171 ± 33	181 ± 6	9.2 ± 0.5	<70	<10	50 ± 17	1.60 ± 0.09
5	Forehead hairline	Washed	540	2.6 ± 0.3	18 ± 1	37 ± 5	205 ± 7	3.0 ± 0.2	185	42	16 ± 4	2.0 ± 0.3
9		None	480	1.2 ± 0.1	<10	55 ± 8	186 ± 7	4.9 ± 0.2	124	41	13 ± 3	1.8 ± 0.2
٢	Nape hairline	Washed	590	0.48 ± 0.01	<8.5	30 ± 8	204 ± 9	4.3 ± 0.2	280	16	18 ± 4	1.55 ± 0.08
80		None	580	5.0 ± 0.1	<8.6	32 ± 5	188 ± 9	6.4 ± 0.3	<70	13	26 ± 3	1.72 ± 0.06
6	Hairline	Washed	570	0.99 ± 0.03	13	31 ± 3	194 ± 9	36 ± 3	238 ± 7	37 ± 4	50 ± 13	1.78 ± 0.27
	over right ear											
10		None	660	0.57 ± 0.06	10.4	45 ± 2	196 ± 8	32 ± 2	296 ± 2	49 ± 8	41 ± 14	1.55 ± 0.20
16	Hairline	Washed	470	0.83 ± 0.04	<11	47 ± 3	215 ± 3	4.1 ± 0.1	<85	20	6	1.80 ± 0.04
	over left ear											

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	g, ppm	日本 1 年 0.02 1 年 0.3	+ 0.3 + 0.6	Table 3a.	,, ppm	+ 0.04	± 0.08	± 0.11 ± 0.43
		1.1 2.2	5.2	air in	ΪĤ	1.80 2.31	2.18	2.70 4.80
	Au, ppb	$<3 < 3 < 3 < 3 < 47 \pm 7 < 47 \pm 7 < 366 \pm 120 < 47 \pm 7 < 56 < 56 < 56 < 56 < 56 < 56 < 56 < $	47 ± 11 120 ± 36	hat for the h	Au, ppb	9 19 + 5	40 ± 7	35 ± 8 61 \pm 15
	Sb, ppb	$32 \\ 29 \pm 2 \\ 35 \\ 35 \\ 35 \\ 35 \\ 35 \\ 35 \\ 35 \\ $	37 ± 8 65 ± 9	fjacent to ti	Sb, ppb	20 23	25 ± 1	$\begin{array}{c} 17\pm2\\ 36\pm3\end{array}$
	Ag, ppb	<pre><70 <70 <70</pre>	400 ± 12 620 ± 20	a position a	Ag, ppb	< 85 (185 + 30)	219 ± 11	$\begin{array}{c} 292 \pm 27 \\ 509 \pm 27 \end{array}$
	Se, ppm	4.3 ± 0.2 33 ± 2 60 ± 3	80 ± 3 87 ± 5	, plucked from	Se, ppm	4.1 ± 0.1 26 + 1	55 ± 2	67 ± 2 85 ± 2
	Zn, ppm	196 ± 6 174 ± 6 179 ± 6	154 ± 4 158 ± 6	anagen hair,	Zn, ppm	215 ± 3 187 + 6	161 ± 6	165 ± 5 175 ± 5
	Co, ppb	44 ± 12 106 ± 10 144 ± 17	201 ± 16 230 ± 14	s of a single	Co, ppb	$\begin{array}{c} 47 \pm 3 \\ 110 \pm 16 \end{array}$	130 ± 6	163 ± 7 230 ± 17
	Fe, ppm	68 ± 3	$\begin{array}{c}18\\18\\20\pm2\end{array}$	cm segment	Fe, ppm	11> 6>	8.8	<7 22 ± 5
	Cr, ppm	1.9 ± 0.1 11.4 ± 0.9 1.08 ± 0.13	0.51 ± 0.05 1.1 ± 0.1	in successive 10	Cr, ppm	0.83 ± 0.04 0.29 ± 0.03	0.75 ± 0.07	0.30 ± 0.01 2.40 ± 0.07
	Prepara- tion	Washed Washed Washed	Washed Washed	icentrations	Prepara- tion	Washed Washed	Washed	Washed Washed
	Segment Weight, μg	560 570 520	550 550	element con	Segment Weight, μg	470 590	670	730 390 (for 6 cm)
	Distance from root, cm	1–11 11–21 21–31	31-41 41-51	3b-Trace	Distance from root, cm	1-11 11-21	21–31	31–41 41–47 (
I	Hair Identi- fication Number	11 12	14 15	TABLE	Hair Identi- fication Number	16 17	18	19 20

evaporation in the capsule of measured volumes of solutions of known concentrations. Also included were weighed amounts of aluminium wire of known cobalt content [20] to act as neutron-flux monitors. These standard samples were distributed spatially among the encapsulated hair samples during the irradiations in order to minimize errors due to spatial variations of neutron flux.

Irradiations and Preparation for Radiation Measurements

Irradiations were conducted in the thermal neutron facilities of the NRU reactor at Atomic Energy of Canada Ltd., Chalk River, Ontario. Fluxes were near $2 \times 10^{14} \text{ n/cm}^{-2}/\text{s}^{-1}$, and irradiation times were between 36 h and 3 days for some experiments and 24 days for others.

After 3 days at these flux levels, the larger hair samples were found to have lost 25 percent of their weight, and to have the appearance of having been extensively charred. The single hairs were shrivelled, and the walls of the quartz capillaries were coated with a brown oily material. The capillary contents were however easily and completely removed by flushing with a few drops of concentrated nitric acid. The capillary then showed only the same γ -radiation spectrum as did an empty irradiated capillary. The nitric acid rinsing of this latter tube dislodged only negligible amounts of γ -radioactivity. The irradiated element standards were not removed from their encapsulation but were measured *in situ*, since the radiation levels from the capillaries were shown to be negligible compared with those from the standards.

For the series A experiments, the larger irradiated sample was transferred to a pestle and mortar, and ground for 15 min into a fine dust. The material was divided into 10 replicate samples, each of which was weighed, after mounting for radiation measurements in plastic capsules.

The smaller irradiated sample was also ground and divided up, for experiments in which Na-removal [21] by means of hydrated antimony pentoxide, and element group separation by substoichiometric extraction techniques [22] were studied. These experiments permitted confirmation of the identification of certain of the radioactivities found in the irradiated hair. The procedures proved too time-consuming however for routine application in the many analyses reported in this paper, and will not be described further.

For the B series of experiments, the irradiated hair material, which had been flushed from the irradiation capsules with nitric acid was transferred to unirradiated plastic capsules for radiation measurements. The irradiated Al/Co neutron monitors were similarly mounted.

Radiation Measurements and Data Reduction

Gamma-radiation energies and intensities were measured by means of a 23.8-cm³ Ge(Li) coaxial detector [23] having a 2.5 to 3.0 keV resolution for the 1332 keV γ -rays from ⁶⁰Co, and calibrated by means of a sample of ²²⁶Ra and its decay products [24]. Conventional electronic apparatus was employed, and the data were stored in the form of 1600-channel spectra. A typical spectrum is shown in Fig. 1.

Three spectrum measurements were made on each specimen at various times between 2.5 and 34 days after the end of irradiation. The spectra were analyzed for peak energies on an IBM 360/50 computer by means of the computer program SAMPO [25], and for peak intensities by means of either the computer program or graphical analysis [26].



FIG. 1—Typical γ -spectrum, measured with a Ge(Li) detector, from a 10-cm segment of a single human head hair, following a neutron irradiation of 24 days duration at a flux of $2 \times 10^{14} \text{ n/cm}^{-2}/\text{s}^{-1}$. The spectrum measurement began 6.7 days after the end of the irradiation, and lasted 3 h.

The observed spectrum peaks were identified by various criteria as arising from particular radioactivities:

- (a) The energy corresponded to a known γ -radiation from a radionuclide product of a (n,γ) or double neutron capture reaction on a naturally occurring nuclide,
- (b) Other γ -radiations from the radionuclide in question were accounted for in relative intensities corresponding to those in the literature,
- (c) The relative γ -intensities observed in spectra taken at different times after the end of irradiation were consistent with the known half-life of the radionuclide.
- (d) The behavior of the radioactivity in the chemical separation experiments corresponded to that reported in the literature.

The half-life and γ -energy values employed in the identification of particular nuclides are listed in Table 4.

Finally the observed γ -intensities were converted to element concentrations, by means of comparison with the irradiated standards, and with correction for the times, sample weights, and other relevant factors in the experiments.

Although the γ -radiations from ²⁴Na and ⁸²Br decay (seen in Fig. 1) were prominent in many spectra measured in this work, Na and Br concentrations were not calculated. This was in the expectation (following earlier work) that these elements would not prove valuable from the hair characterization point of view.

homogenized hair.
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4Trace
TABLE

					Compi	rter calculate	d areas	Covell's meth	nod of calcula	ting areas [26]
Element	Nuclide	Half-life	Energy of γ-ray, keV	Number of samples used in calculation of statistics	mdd	Standard deviation	Relative Standard Deviation, 7%	udd	Standard deviation	Relative Standard Deviation, %
Chromium	⁵¹ Cr	27.8 days	320.0	10	0.530	0.138	26.0	0.568	0.105	18.5
		•		8 (Omit 2 points)	0.475	0.083	17.5	0.525	0.060	11.4
Cobalt	°0Co	5.26 years	1173.2	10	0,084	0.009	11.4	0.079	0.008	10.3
Zinc	65Zn	245 davs	1115.4	10	161.5	14.1	8.8	167.1	11.9	7.1
	l			9 (Omit 1 point)	165.1	9.1	5.5	170.8	2.1	1.2
Antimonv	124Sb	60.2 days	603	10	0.061	0.013	21.2	0.064	0.010	15.8
)			8 (Omit 2 points)	0.060	0.006	10.4	0.063	0.003	4.7
			1691	5	0,063	0.012	19.6	0.062	0.003	5.5
Antìmony	122Sb	2.8 days	564	10	0.065	0.013	20.3	0.067	0.012	17.4
Selenium	75%	120 davs	121	10	0.720	0.132	18.3	0.712	0.087	12.2
	2		136	10	0.702	0.110	15.7	0.725	0.076	10.4
				(265 keV also employe	ed in single h	air analyses)				
Silver	110 mAg	255 days	658	10	0.275	0.038	13.9	0.307	0.044	14.3
Bromine	^{82}Br	35.34 h	554	10			5.6			
	l		619	10			4.6			
			698	10			12.4			
			LTT L	10			5.9			
Mercury	203Hg	47 days	279 -	10	1.243	0.029	2.4			
Iron	59Fe	45 days	1292	6	20.02	3.01	15.1	25.41	2.66	10.5
		•		7 (Omit 2 points)	19.69	2.10	10.7			
			1099 ه	8	26.89	2.14	7.9			
Gold	198 A u	2.8 days	412	10	0.0267	0.0046	17.2			
				9 (Omit 1 point)	0.0253	0.00166	6.5			
Calcium	47Ca	4.7 days	1297.7°	6	333.59	58.28	17.5			
Scandium	⁴⁶ Sc	84 days	889	9	0.0022	0.00012	5.6			
 Values cc Values cc Values cc 	prrected for el prrected for el prrected for ef	The form of 76 Se γ^{-1} fields of 65 Zn γ^{-1} fields of 69 Fe γ^{-1}	ray which is c ray which is ray which is	lose-by in energy. close-by in energy. close-by in energy.						
			•							

Results

Series A

These experiments were directed toward determining the ability of the present technique to reproduce trace element concentrations, by analysis of the 10 replicate samples of ground, irradiated hair. The error was expected to be smaller for the elements for which the γ -intensities were larger and vice versa due to statistical uncertainties in the data. The results are shown in Table 4.

It is seen that the relative standard deviation in the concentration values obtained by computer reduction of the data range from ± 2.4 to ± 26.0 percent; the smallest values perhaps indicating the degree of success of the grinding procedure in producing a homogeneous material, while the largest reflect the effects of statistical uncertainties in the data on the ability of the computer program to correct peak areas for the background effects of spectrum continua. It was found that better results were obtained when Covell's method [26] of graphic analysis was employed. These are also shown in the data of Table 4 and were subsequently adopted for the series B measurements.

Generally the table suggests that the presently reported data are good to better than ± 10 percent in relative value in many cases and ± 20 percent in all; however the reduced intensities in the series B experiments may have resulted in some results of lower quality although this would have been difficult to verify.

In addition, it is estimated that for those element determinations where the above experiment indicated a relative precision of better than ± 10 percent, various other factors would have limited the absolute accuracy of the determinations to a worse figure.

Series B

The first experiments on analysis of single hairs were directed towards determining which elements could be measured with the irradiation and decay times previously employed, and also towards some study of the problems of hair washing. Six hairs were plucked from various locations on the head of female subject B, but were not sorted as to whether they were in the anagen or telogen phases of the hair growth cycle. The hair locations are listed in Table 1. Hair number 1 and hair number 2 were plucked from adjacent positions on the scalp. As also indicated in Table 1, certain hairs were subjected to the washing with boiled, distilled, deionized water described earlier. Following drying and encapsulation the hairs were irradiated with a neutron flux of 2×10^{14} n/cm⁻²/s⁻¹ for 3 days; after the 2 to 3 day delay for transport to the laboratory, 3 elements could be determined to satisfactory statistical precision, namely, zinc, selenium, and gold. The concentrations found are listed in Table 1.

The results indicate that while the zinc concentrations fell within a factor of 2 for all of the hairs examined, the selenium and gold concentrations varied considerably from one end of a hair to the other, namely by a factor of 3 in the case of selenium and a factor of 10 in the case of gold. The selenium and gold concentrations also varied with hair location on the head, the hairs taken from the nape or rear of the head tending to show the higher concentrations.

The data also contained some slight indication that the water washing procedure tended to raise the concentrations of selenium and gold. This is difficult to understand except in terms of the hair picking up additional quantities of such rare trace elements from the highly purified washing water [18]. However, it was decided to explore another hair cleaning procedure.

Additional single hairs were therefore plucked from the head of the same female subject B, 6 months after the first experiments. They were taken in groups from five locations: the crown, the hairline at the forehead, the hairline at the nape or back of the head, and at the hairline over the left and right ears. The hairs were then sorted as to anagen or telogen phase after the first 1 cm adjacent to the root was cut off. The hairs were then cut into 10-cm segments; for some hairs only the first 10-cm segment adjacent to the root was retained, while for others all the segments from the root to the end were used. Certain hairs were subjected to the washing procedure involving ether, acetone, and water as described earlier. The particular details for the hair segments employed in this experiment are listed in Tables 2 and 3.

These hairs, after encapsulation, were subjected to a 3-week neutron bombardment at the same flux as before. Following their return to the laboratory, nine elements could now be determined as listed in Tables 2 and 3. In six out of the nine elements studied, two or three concentration values could be calculated from spectra taken at different times after the end of bombardment. These several values were averaged to produce the values displayed in Tables 2 and 3. The errors listed with these numbers indicate the spread between the several values obtained.

Examination of the concentration data in the tables reveals the following:

Hair Washing—There is no longer evident a marked tendency for the concentration values in the hair washed by the ether-acetone-water procedure to be higher or lower than those in related but untreated hair. Presumably this means that the hair was not being significantly contaminated during the washing procedure or that the technique employed is effective in removing almost all the adventitious contamination or both. The similarity of the values for treated and untreated hair may perhaps indicate that the hair was relatively clean when it was plucked.

Location—Hair numbers 1, 2, 3, and 4 were taken from immediately adjacent positions on the scalp and were all identified as being in the anagen stage. The analytical data in Table 2 are for hair segments between 1 and 11 cm only from the scalp. Thus, from these three facts one would expect the hairs to be similar in their nutritional history and exposure to contamination. One observes that, for the hairs that had been washed, while the cobalt, zinc and mercury concentrations in all three are very similar, the chromium, iron, selenium, and gold concentrations vary by as much as a factor of two, and a greater variation is seen in the case of antimony and silver.

If one includes in the comparison hairs 5, 7, 9, and 16, one observes that concentration variations for hairs taken from nonadjacent sites on the head are somewhat larger. Thus, for example, the spread in gold and chromium values is now a factor of 5 and in selenium values a factor of 10.

Hair Growth Cycle—In Tables 3a and 3b and in Fig. 2 one is able to compare concentrations in hairs plucked from adjacent scalp sites, one hair identified as being in the anagen phase and one in the telogen phase. Inspection of these data indicates that while the concentrations at particular positions along the hair tend, in a hair in the telogen phase, to be higher than one in the anagen phase, the differences appear to be no greater than those between hairs which were all in the anagen phase, Table 2. It is possible that the hair growth cycle had had relatively little effect on the trace element concentrations in these hairs, or that the particular telogen hair in Table 3a had, by chance, only recently entered that phase. It would then be expected to display trace element concentrations similar to those found in an anagen hair. Such possibilities can only be distinguished by further experimentation.



FIG. 2-Variation of trace element concentrations as a function of distance from the scalp.

Variation Along the Length of a Hair—Tables 3a and 3b, and Fig. 2 indicate a considerable variation in the trace element content as one moves from the scalp to the outer end of the hair. In Fig. 2 concentrations in the hair identified as telogen are indicated by T, those in the anagen phase hair by A, and those for hairs 1 and 2 in Table 1 are indicated by I (the phase in the growth cycle for these hairs not having been determined). One observes for the telogen hair that the chromium, iron, and gold concentrations between 11 and 21 cm from the scalp were extremely high compared with concentrations in adjacent segments, while at the same time the other element concentrations for this segment did not appear exceptional. With the exception of these high values, however, there is a general trend for all elements other than zinc to increase in concentration from the scalp to the outer end of the hair. The increase ranges from about a factor of 2 in several cases to more than a factor of 20 in the case of selenium. Only in the case of zinc is there a decrease in concentration from the scalp outwards and then by about 25 percent or less. There is no evidence of any particular effect beyond about 20 cm from the scalp produced by the cream rinses applied by the subject to that region of the hair.

The elements cobalt, zinc, and mercury which displayed the least variation as a function of geographic position on the head, also display the greatest similarity between the concentration values for the hair in the telogen phase and that in the anagen phase at each 10-cm segment from the root to the end of the hair. In the case of zinc, as has been noted, the concentration variation from one end of the hair to the other is small. In the case of cobalt and mercury, however, it is substantial. Whatever the cause of this concentration variation, whether it be strictly the effect of hair nutrition or the effect of contamination of the hair from sweat and external sources, the pattern displayed for cobalt, zinc, and mercury may perhaps be characteristic of the subject concerned. Further experiments should be able to clarify this. The data for the remaining six elements, however, exhibit fluctuations which tend to conceal any specific pattern. Overall Single Hair Variations—Since an important factor determining the possibility of single hair characterization is liable to be hair to hair variations on the scalp of a single subject, it was decided to pursue this aspect of the analysis further. The twenty 10-cm hair segments represented in Tables 2, 3a, and 3b were treated as independent samples, as might be encountered in a forensic application and where location on the scalp, distance from the scalp end, and phase in the hair growth cycle might be undeterminable. Figure 3 shows the distribution of the concentration values in single hairs for the nine elements determined here compared with those reported in the literature [6] for larger hair samples taken from many people in the population at large. Although the statistical precision of a distribution obtainable with twenty samples is quite limited, the comparison is perhaps interesting. It is presented with the reservation that the two sets of data were obtained via quite different techniques, at times 5 years apart, and refer to a subject resident in British Columbia on the one hand, and to subjects resident several thousand miles further east on the other.

In the case of chromium, iron, cobalt, zinc, and mercury, the two sets of data have been compared without normalization. In the case of selenium, silver, antimony, and gold, however, since the comparison of distribution ranges was of prime interest, the concentration scales have been normalized to facilitate such a comparison. Thus, in the case of antimony, for example, the present concentration values were found to lie in the range of a few tens of parts per billion (that is, parts per 10⁹), while the most probable concentrations



FIG. 3—Distribution of trace element concentrations among twenty hair samples in the present study, compared with the concentration distributions for the population at large.

for the population at large were reported to lie in the range of several parts per million. While the present values did not lie outside the range found for the population at large, in Fig. 3 the present data have been plotted on a concentration scale one thousand times wider than that for the population at large. The 20 parts per million point for the distribution of the population at large is marked in Fig. 3 for clarity and similarly for each of the other elements for which a similar scale shift was made.

The general conclusion from the figure may be that, with the exception of zinc, the range of distribution of concentrations in single hairs is comparable with that for hair samples taken from the population at large. However, this effect is due in part to the variation of concentration shown in Fig. 2 from one end of the hair to the other. To remove this effect, but at the risk of yet poorer statistics, the data in Table 3 for washed hair segments between 1 and 11 cm from the scalp were plotted separately in Fig. 3 and are shown as the solid histogram. The conclusion for zinc is essentially unchanged but, in the case of cobalt and mercury, the distribution range for single hair segments between 1 and 11 cm from the scalp of a single individual is seen to be much narrower than that reported for hairs taken from the population at large. For the other six elements however the range of the distribution, as far as it can be determined, is still comparable to that reported for the population at large.

Conclusions

This study has demonstrated the feasibility of measuring the concentrations of at least nine elements in 10-cm segments of individual human hairs by the techniques of instrumental neutron activation analysis. No particular concentration differences were revealed between hairs in the anagen and telogen phases of the growth cycle. Of the elements studied, six showed hair to hair variations comparable in magnitude for that reported earlier for hair taken from the population at large.

In the case of three elements however, namely cobalt, zinc, and mercury, whose origins and significance remain unknown, individual hair segments between 1 and 11 cm from the scalp of a single subject showed variations in concentration much smaller than those reported for the population at large. Further, the variation in concentrations in hair segments between 1 and 51 cm from the scalp were closely similar for a telogen and anagen hair plucked from the scalp at the same time, although the variations for these three elements were in fact different in pattern.

Thus, some of the criteria for successful hair characterization may perhaps be satisfied in the case of these latter three elements. Confirmation of such a conclusion and the discovery of further elements for which the criteria are satisfied must await further experimentation with other subjects. This must then be followed by successful characterization attempts in the laboratory and in the field before more firm conclusions are drawn regarding the feasibility of identifications by single hair analyses such as those described herein.

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References

- [1] Kirk, P. L., Proceedings of the First International Conference on Forensic Activation Analysis, V. P. Guinn, Ed., Gulf General Atomic Inc., San Diego, Calif., 1967, p. 41
- [2] Perkons, A. K. and Jervis, R. E., Modern Trends in Activation Analysis, Vol. I, National Bureau of Standards Special Publication 312, Washington D.C., 1969, p. 256.
- [3] Bate, L. C. and Dyer, F. F., Proceedings of the First International Conference on Forensic Activation Analysis, V. P. Guinn, Ed., Gulf General Atomic, Inc., San Diego, Calif. 1967, p. 247.
 [4] Parker, J. B., Journal of the Forensic Science Society, Vol. 6, 1966, p. 33.
 [5] Parker, J. B., Journal of the Forensic Science Society, Vol. 7, 1967, p. 134.
- [6] Perkons, A. K. and Jervis, R. E., Proceedings of the Second International Conference on Modern Trends in Activation Analysis, Texas A&M University, 1965, p. 295.
- [7] Perkons, A. K. and Jervis, R. E., Journal of Forensic Sciences, JFSCA, Vol. 11, 1966, p. 50.
- [8] Coleman, R. F., Cripps, F. H., Stinson, A., and Scott, H. D., Proceedings of the First International Conference on Forensic Activation Analysis, V. P. Guinn, Ed., Gulf General Atomic Inc., San Diego, Calif., 1967, p. 203.
- [9] Coleman, R. F., Journal of British Nuclear Energy Society, Vol. 6, 1967, p. 134.
- [10] Bate, L. C. and Dyer, F. F., Nucleonics, Vol. 23, 1965, p. 74.
 [11] Kerr, F. M., M.Sc. Thesis, University of Ottawa (1964).
- [12] Jervis, R. E., Perkons, A. K., Mackintosh, W. D., and Kerr, M. F., Proceedings of the 1961 International Conference on Modern Trends in Activation Analysis, Texas A&M University, 1961, p. 107. [13] Perkons, A. K. and Jervis, R. E., Journal of Forensic Sciences, JFSCA, Vol. 7, 1962, p. 449.
- [14] Lima, F. W., Shibata, H., and Atalla, L. T., Symposium on Radiochemical Methods of Analysis, IAEA Vienna, Vol. 1, 1965, p. 119.
- [15] Erickson, N. E., Krishnan, S. S., and Perkons, A. K., Proceedings of the Fifth International Criminological Conference, Montreal, 1965.
- [16] van den Berg, A. J., de Bruin, M., and Houtman, J. P. W., Nuclear Activation Techniques in the Life Sciences, IAEA Vienna, 1967, p. 661.
- [17] Bate, L. C., Journal of Forensic Sciences, JFSCA, Vol. 10, 1965, p. 60.
- [18] Bate, L. C., International Journal of Applied Radiation and Isotopes, Vol. 17, 1966, p. 417.
- [19] Prokop, Sgt. T. J., Royal Canadian Mounted Police, private communication, 1970.
- [20] Standard Reference Material SRM 953, National Bureau of Standards, Washington, D.C.
- [21] Giradi, F. and Sabbioni, E., Journal of Radioanalytic Chemistry, Vol. 1, 1968, p. 169.
- [22] Elek, A., Boganes, J., and Szabo, E., Journal of Radioanalytical Chemistry, Vol. 4, 1970, p. 281.
- [23] Oak Ridge Technical Enterprises Corp., Oak Ridge, Tenn. [24] Lingeman, E. W. A., Konijn, J., Polak, P., and Wapstra, A. H., Nuclear Physics, Vol. A133, 1969, p. 630.

[25] Routti, J. T. and Prussin, S. G., Nuclear Instrumentation and Methods, Vol. 72, 1969, p. 125.

[26] Covell, D. F., Analytical Chemistry, ANCHA, Vol. 31, 1959, p. 1785.

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