

## The Absorption of Mercuric Ion into Single Human Head Hairs

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**REFERENCE:** Mackintosh, J. and Pate, B. D., "The Absorption of Mercuric Ion into Single Human Head Hairs," *Journal of Forensic Sciences*, JFSCA, Vol. 27, No. 3, July 1982, pp. 572-591.

**ABSTRACT:** The concentration patterns of radioactive  $\text{Hg}^{++}$ ,  $\text{Cu}^{++}$ , and  $\text{I}^-$  in individual hair shafts, after soaking in aqueous solutions of these tracers, were measured nondestructively to permit repeated experiments on a given shaft. The mercury concentrations generally increased from the root end to the distal end of a given shaft less steeply than those of copper, while iodide concentrations generally decreased. Concentration peaks and other pattern features for mercury were also relatively less intense, but there was some correlation of the position of such areas of increased mercury, copper, and iodine adsorption in a given shaft. At equilibrium after more than 100 h of soaking, the amount of mercury taken up at pH 8 by the hair was three to four times that at pH 3. The rate of absorption of mercury was higher at low pH values, and that of desorption higher at high pH values. The relative intensity of pattern features remained constant during absorption or desorption at a given pH, but changed if the pH was changed. These data are discussed in terms of the chemistry of the hair binding sites for cations and anions.

**KEYWORDS:** pathology and biology, hair, mercury, trace-element chemistry

Previous papers in this series have dealt with the absorption into human hairs of copper [1], zinc [2], arsenic [3], and phosphorus [4]. The present work began a study of mercury absorption, of particular interest in a medical and environmental context. [5,6].

To avoid the hair-to-hair chemistry variations observed with samples taken from a single human subject [1], a technique was employed in the present work that had been developed in a previous study [4]. It permitted the nondestructive assay of radioactivity in approximately 2-mm sections of a single hair shaft by scanning down the shaft with a surface barrier beta-radiation detector (ORTEC Model BA-24-300-300), collimated to a 2-mm diameter by a lead collimator 2 mm thick. Thus, a single hair could be subjected to repeated manipulations (soaking, rinsing, and so on), with radioactivity scans interposed, to follow the tracer concentration changes produced. The hairs studied were almost all drawn from the same 23-year-old female subject to avoid, at least for this study, the person-to-person variations observed previously [1]. The only exceptions were those used in the bleaching experiments reported below.

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## Techniques

Hair samples were plucked rather than cut to allow growth-cycle phase determinations by microscopic examination of the root. Hairs plucked while in the anagen, or growing, phase of the cycle were recognized through their dark, plump root bulbs and white root sheaths. Only anagen hairs were employed in this study. They were individually washed by means of the ether-acetone-water cycle previously described [1] and then air-dried and sealed in glass or plastic vials until needed. Samples of  $^{203}\text{Hg}$  radioactivity, as mercuric nitrate solution, were obtained from New England Nuclear Corp., Billerica, MA, and had a specific activity of 2.4 to 4.2 curies per gram of mercury. Samples of  $^{67}\text{Cu}$  were obtained through the courtesy of Atomic Energy of Canada Ltd. (AECL) at TRIUMF, Vancouver, B.C., and were of no-carrier-added quality. The  $^{131}\text{I}$  originally supplied by AECL was carrier-free and was obtained through the courtesy of Dr. Donald M. Lyster of Vancouver General Hospital, Department of Nuclear Medicine.

Unless otherwise noted, the mercury tracer solutions prepared for the following experiments had concentrations in the range from 50 to 110  $\mu\text{Ci}$  of  $^{203}\text{Hg}$  per millilitre and of 0.037 to 0.092 mg of mercury per millilitre, while the  $^{131}\text{I}$  and  $^{67}\text{Cu}$  solutions had concentrations of 0.6 mCi/mL and 0.4 mCi/mL, respectively.

The pH values required for a given experiment were determined with a pH meter and were controlled either by application of the buffer solutions noted below or by careful neutralization of the initial tracer solution with sodium hydroxide or nitric acid solution and dilution to the required volume. During the course of the experiments, the tracer solution concentrations varied within the above ranges because of absorption by the hairs themselves, the addition of reagents to maintain the required pH, and the chemical manipulations involved. The potential effect of these modest concentration changes was examined in the case of  $^{203}\text{Hg}$  tracer in an experiment described below.

Following soaking in tracer solution, with care taken to ensure complete submersion, each hair was removed by means of Teflon<sup>®</sup>-coated forceps and subjected to two 1-min rinses with distilled water to remove superficial tracer solution. The experiments described below showed that exposure for this length of time to distilled water did not appreciably affect, for example, the mercury concentration pattern in the hair. The rinsed hair was then placed between fresh filter paper sheets to dry.

The hair was then aligned with the minimum tension along a fiducial line on a Lucite<sup>®</sup> mounting block for scanning and was covered for protection with Saran<sup>®</sup> plastic film and Scotch<sup>®</sup> tape of 0.08-mm total thickness. The radioactivity pattern in the hair was then obtained by the above-mentioned scanning procedure; automatic data acquisition equipment permitted the scanning to proceed conveniently unattended and for long enough to acquire good statistical precision. Generally more than 1000 decay events were measured per 2-mm hair segment, and the data were corrected for decay during the experimental procedure by means of the known half-life values [7].

## Results

### *Validity of the Radioactivity Assay Procedure*

Two single hairs were soaked in  $^{203}\text{Hg}^{++}$  tracer solution and then subjected to a series of mounting, scanning, and unmounting cycles. The radioactivity concentrations measured in five and seven cycles in each case were within the limits expected from the statistical precision of the data and from the effects of the detector scanning motion along the hair shaft. Thus, confidence was achieved in the ability of the technique to reproduce the relative intensity of the activity measured in the same region of a given shaft and in different 2-mm shaft segments. One of the two hairs was then cut into 1-mm segments, chosen to correspond in

location to the regions studied in the scanning procedure, and the segments were individually assayed in a constant counting geometry under the semiconductor detector with the collimator removed.

The results are shown in Fig. 1, and the radioactivity concentration pattern so determined was compared with one of those measured by the scanning technique. It is seen that the scanning procedure (A in Fig. 1) smooths out somewhat the millimetre-to-millimetre radioactivity fluctuations measured in the individually cut segments (B in Fig. 1), which are similar to those observed in the absorption of other elements [1,2]. Otherwise, the magnitudes of the pattern features are closely similar in the results from the two procedures and are located at closely similar distances from the hair root (always recognizable by its intense absorption of tracer).

#### *Effect of $Hg^{++}$ Concentration Changes*

In two experiments, two individual hairs were first soaked for identical times in one tracer solution, then subjected to a radioactivity scan (see A and C in Fig. 2), then soaked in a second tracer solution again for identical times, and finally subjected to a second radioactivity

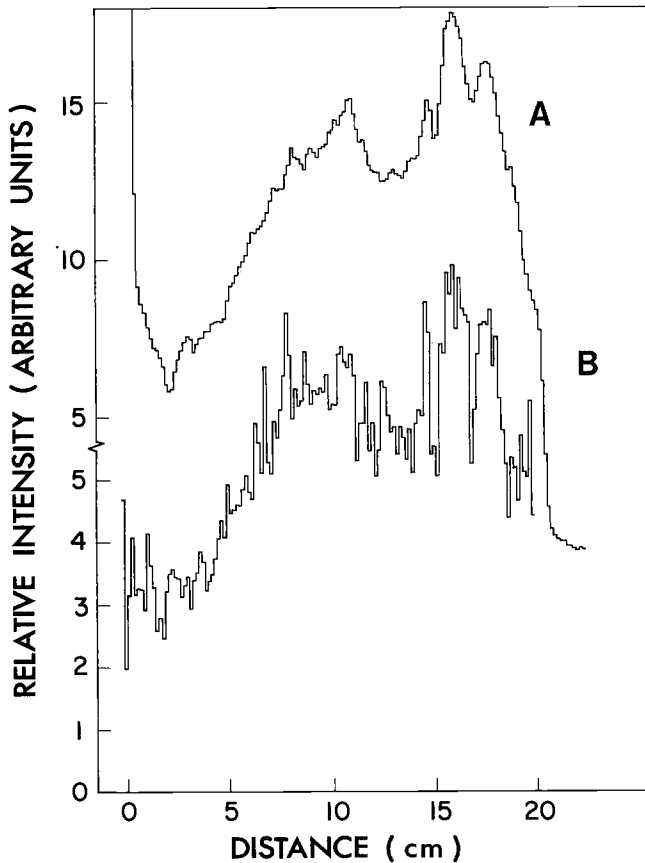


FIG. 1—Comparison of tracer concentration profiles measured (A) by the scanning technique and (B) by individual 1-mm segment radioassay.

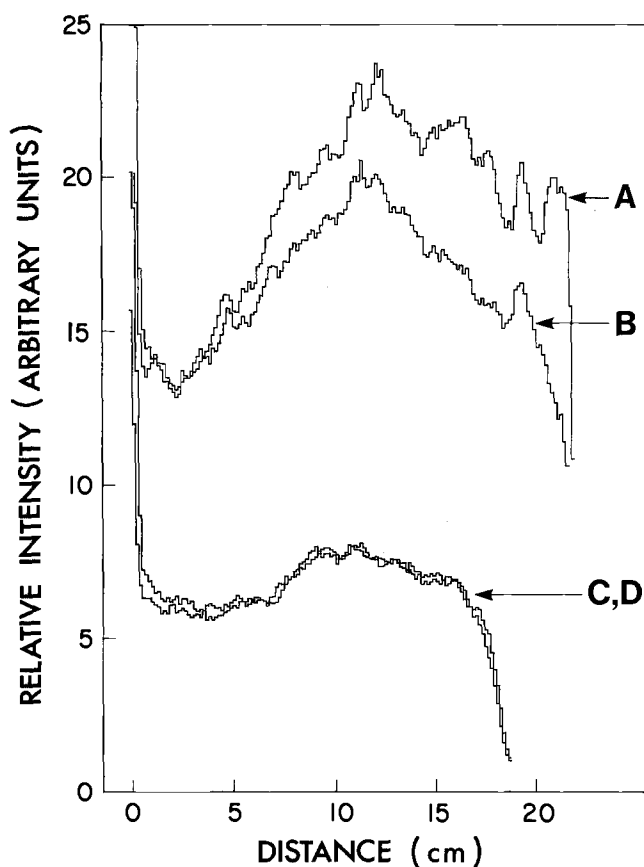


FIG. 2—Study of the effect of successive hair soakings in solutions of different concentrations: (A) Hg radioactivity concentration profile after initial soaking in a dilute Hg solution, (B) profile in the hair from (a) after soaking in a more concentrated Hg solution, (C) Profile in a second hair after initial soaking in a more concentrated Hg solution, and (D) profile in the hair from (c) after a subsequent soaking in a more dilute Hg solution.

scan (see B and D in Fig. 2). The order of application of the two solutions was reversed in the two experiments. In one solution the mercury concentration (obtained by simple dilution of the supplied stock solution) was 0.028 mg/mL, while in the other the mercury concentration for the same tracer concentration was increased tenfold (to 0.30 mg/mL) by the addition of "cold" mercuric nitrate solution. In each case, the pH was maintained near 5.5 with phthalate buffer (see below).

The results of the four scans (Fig. 2) indicate that application first of the solution dilute in mercury (followed by Scan A) and then of that more concentrated in mercury (followed by Scan B) produced up to a 20% decrease in the relative activity of the sample, indicating displacement of some of the absorbed tracer by cold mercury. However, an application of a concentrated mercury tracer solution (Scan C) followed by that of a dilute solution (Scan D) produced no appreciable intensity change. The results confirm that concentration changes within the ranges produced by the experimental manipulations, as noted earlier, did not by themselves produce changes in the concentration pattern large enough to mask the influence of the experimental parameters being studied.

*Stability of the Hg<sup>++</sup> Concentration Pattern*

A series of experiments was designed to study the variation in the mercury radioactivity pattern produced by changes in the tracer solutions pH values and soaking times. Before such experiments were begun, however, verification was needed that the mercury in the hair resulting from a soaking procedure was not in a form (metallic, for example) such that mercury loss from the hair would be expected from volatilization. A secondary consideration was that, should volatilization prove to be extensive at elevated temperatures, it might represent a means of decontaminating hair between experiments.

The results of the experiments (in which mercury-loaded hairs were heated) are shown in Fig. 3. The pattern of the concentration of mercury tracer produced by the original soaking operation was found to have changed very little following a 20-h heating of the hair at 80°C. A heating of 6½ h at 140°C did indeed produce a further loss of mercury from the hair (as seen in Fig. 3); however, the results suggest that the loss of mercury by volatilization from hair at room temperature is negligible. On the other hand, the rate of mercury loss at temperatures low enough to retain the integrity of the hair shaft structure was sufficiently slow that it did not represent a useful way of decontaminating hair shafts between experiments.

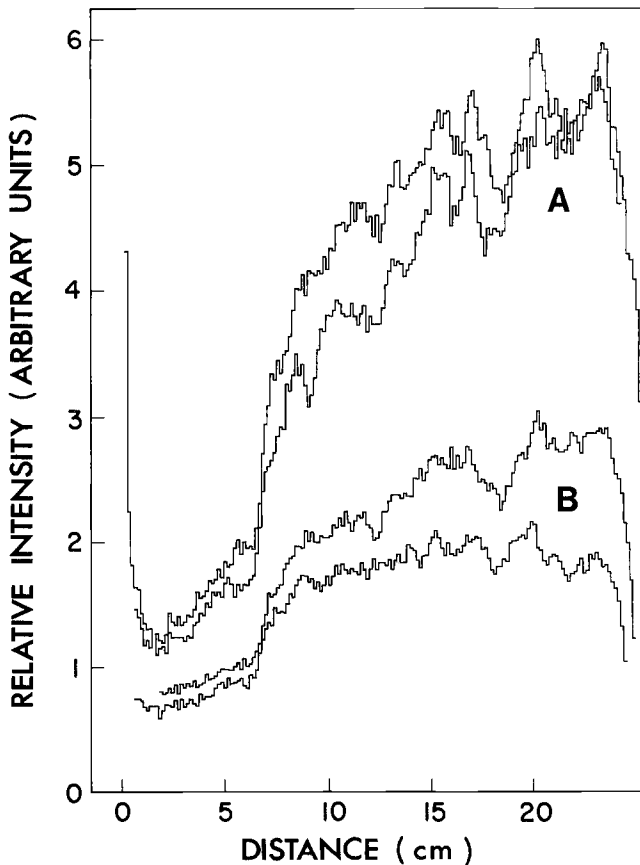


FIG. 3—Volatilization of absorbed Hg from individual hairs: (a) radioactivity profiles before and after a 20-h heating at 80°C and (b) radioactivity profiles before and after a 6½-h heating at 140°C.

*Spatial and Time Variations*

A series of experiments was undertaken to study the changes observed in uptake patterns of mercury tracer in a series of individual hair shafts as a function of soaking time and of the pH of the tracer solution. Two sets of experiments were mounted, each with solutions at values of pH near 3, 5.5, and 8. In one set of experiments the pH values were maintained at these values by glycine, phthalate, and tris(hydroxymethyl)aminomethane buffer solutions, respectively [8], while in the other set of experiments the pH values were adjusted by the titration procedure referred to earlier. No marked difference between the concentration patterns observed (beyond that expected from hair-to-hair variability) could be attributed to the different techniques for pH adjustment.

Figures 4 and 5 show the mercury concentration patterns measured in individual hair shafts soaked for progressively longer times in solutions of the indicated pH. The intensity of the patterns increased with time, initially rapidly and later less rapidly, with the increase in pattern intensity essentially coming to a halt after several hundred hours of soaking. The relative intensity of the pattern features are, however, relatively invariant during this sequence of events: the relative depth of the valleys or height of the peaks in the patterns remains essentially unchanged.

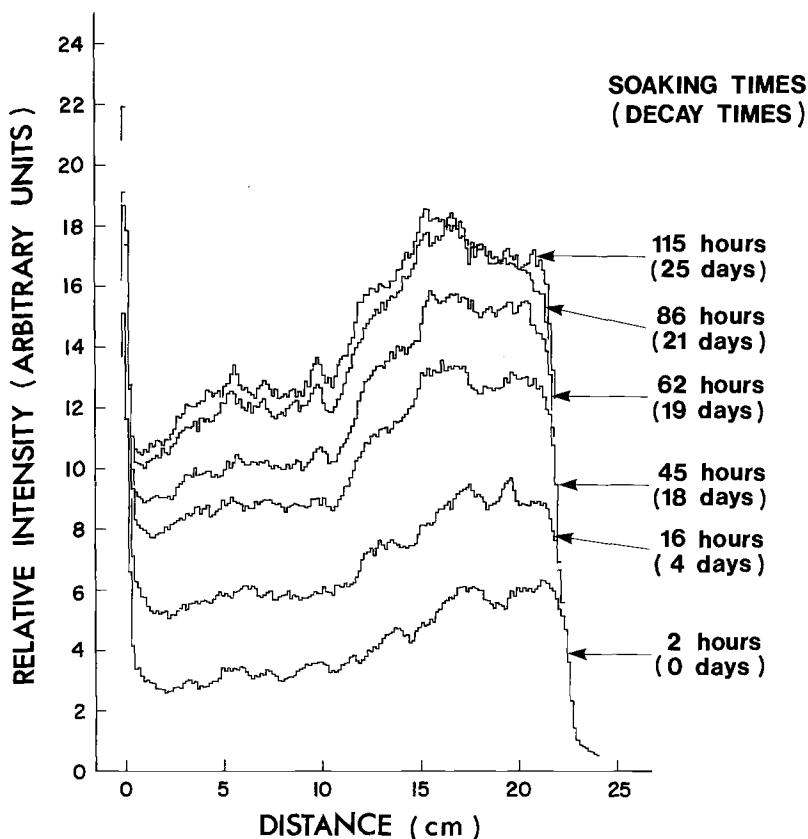


FIG. 4—Absorption of radioactive  $\text{Hg}^{++}$  by a single hair shaft from tracer solution maintained at pH 8 by tris-(hydroxymethyl)aminomethane buffer. The profiles were measured after the indicated total soaking times; the results do not reflect correction for the indicated total radioactivity decay times.

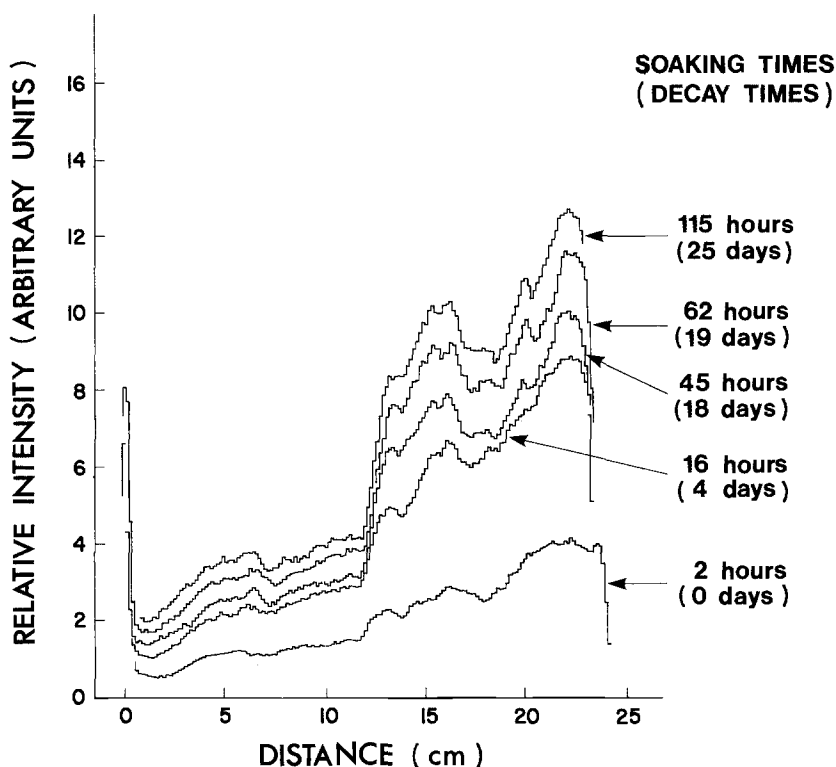


FIG. 5—Absorption of radioactive  $Hg^{++}$  by a second single hair shaft from tracer solution at pH 8, but without buffer solution. The profiles were measured after the indicated total soaking times; the results do not reflect correction for the indicated total radioactivity decay times.

The general form of the variation of the intensity in a given region of the hair with time was found to be given by:

$$y = y_1 - y_2 e^{-at}$$

where

$y$  = pattern intensity,

$e$  = base of natural logarithms,

$y_1, y_2, a$  = constants for a particular region of a particular hair, and

$t$  = the elapsed soaking time.

The constants  $y_1$  and  $y_2$  were found for best fit to the data to be roughly, but not exactly, equal.

The total mercury tracer intensity measured in selected regions of the hair shaft was plotted as a function of time, as shown in Fig. 6, and then fitted to the above functional form by the method of least squares to extract values for the absorption "half-time"  $t_{1/2}$ , which is equal to  $(\ln 2)/a$ . The values thus extracted are shown in Table 1. The data suggest that absorption of mercury into hairs occurs more rapidly at low pH values than at high ones, but no significant variation of half-time with distance down the shaft can be determined from these data.

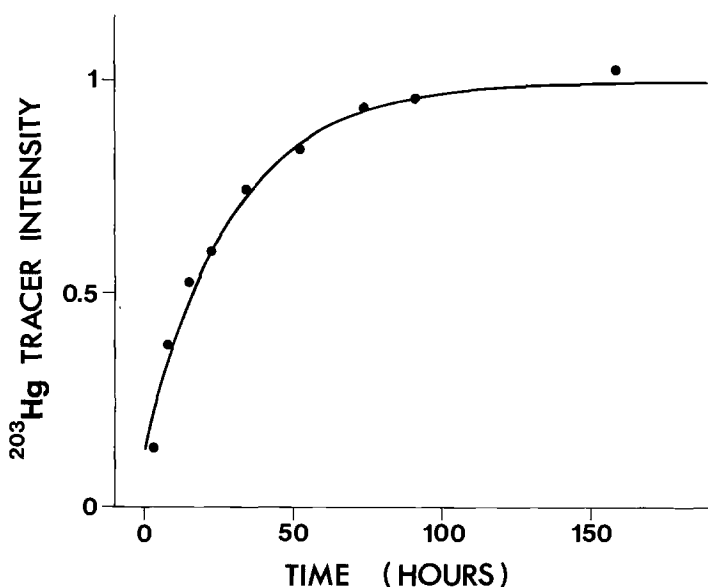


FIG. 6—Typical variation of Hg radioactivity in a selected region of a hair shaft as a function of soaking time in a Hg tracer solution. The line is a least squares fit of the function described in the text.

TABLE 1—Half-times (hours) for absorption into hair of <sup>203</sup>Hg<sup>++</sup>.

pH	Root Section <sup>a</sup>	Midsection <sup>a</sup>	Distal Section <sup>a</sup>
3 (by buffer)	22 ± 2	34 ± 5	31 ± 6
5.5 (by buffer)	28 ± 4	37 ± 5	27 ± 5
8 (by buffer)	38 ± 4	32 ± 4	31 ± 4
3 (by titration)	25 ± 5	9.4 ± 1 <sup>b</sup>	10 ± 2 <sup>b</sup>
8 (by titration)	55 ± 7	64 ± 12	68 ± 11

<sup>a</sup>The root section is approximately 2 to 6 cm from the root, the midsection 11 to 15 cm, and the distal section 15 to 22 cm.

<sup>b</sup>All but the root section of this sample was damaged after 60 h of soaking time; the data points for all sections up to that time gave low  $t_{1/2}$  values. The root section was soaked a further 17 h, giving an extra point, which raised the  $t_{1/2}$  value to the tabulated value.

#### Desorption of Hg<sup>++</sup> Tracer

Next, experiments were conducted to study the rate at which mercury tracer was removed from hairs when they were immersed in nonradioactive rinsing solutions consisting of distilled water plus the reagents needed to maintain pH values near 3, 5.5, and 8.

Contact with the rinsing solutions caused a reduction in the intensity of the mercury concentration patterns in the hair shaft but, again, without a change in the relative intensity of the pattern features, as is shown in Fig. 7. This figure also shows that the initial contact with the rinsing solution produced a relatively rapid decrease in the pattern intensity; later the changes slowed down with increasing exposure to the rinsing solution. Matsumoto [9] found desorption of mercuric chloride from hair to be low when washing with hydrochloric acid was performed.



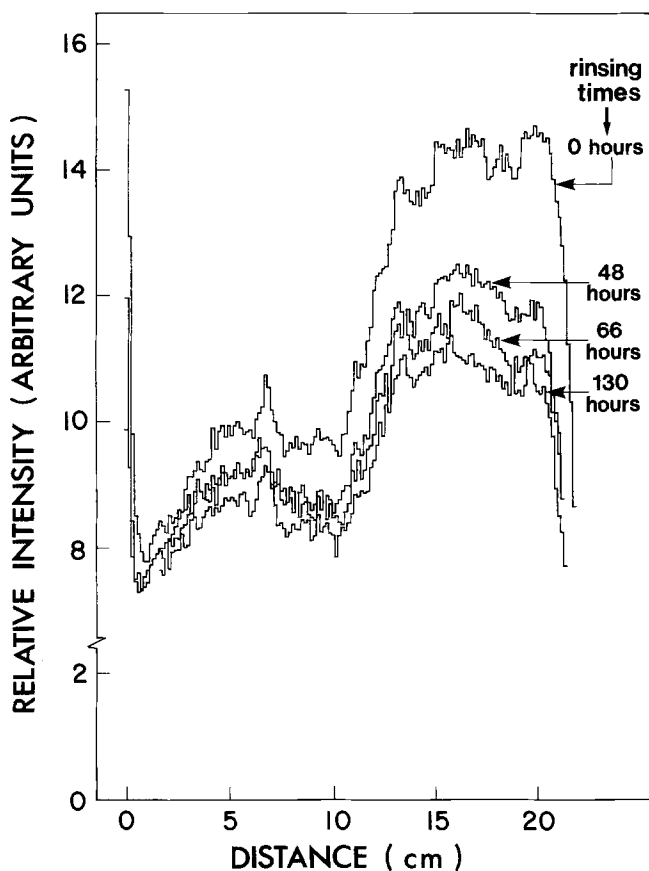


FIG. 7—Desorption of radioactive  $\text{Hg}^{++}$  from a single hair soaked for the indicated total times in distilled water adjusted to pH 8 by means of tris(hydroxymethyl)aminomethane buffer.

The variation of the total activity in various portions of the hair shaft was found in these experiments to follow an approximately exponential form; that is,

$$z = z_0 e^{-bt}$$

where

$z$  = concentration of tracer,

$z_0$  = its value at zero time,

$b$  = constant for a particular segment of a particular hair shaft, and

$t$  = the exposure time.

The data, such as those shown Fig. 7, were used to extract data on the total mercury activity in particular regions of the hair shaft as a function of time, and these were plotted with a semilogarithmic ordinate, as shown in Fig. 8. Also shown in that figure is a fit of a function of the above form by means of the least squares technique. The values for the time for one-half desorption ( $t_{1/2}$ ), which is related to the slope  $b$ , are shown in Table 2. The data suggest the desorption of mercury from hair occurs somewhat more rapidly at high pH values than at low ones, and more rapidly at increasing distances from the root.

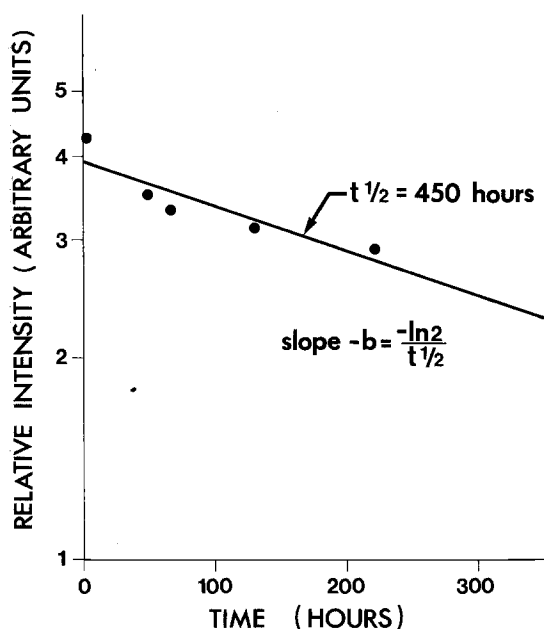


FIG. 8—Typical semilogarithmic plot of the intensity of  $\text{Hg}^{++}$  radioactivity in a portion of a single hair shaft as a function of time of soaking in distilled water maintained at a specific pH value. The line is a least squares fit, as described in the text.

TABLE 2—Half-times (hours) for desorption from hair of  $^{203}\text{Hg}^{++}$ .

pH	Root Section <sup>a</sup>	Midsection <sup>a</sup>	Distal Section <sup>a</sup>
3	1600 ± 500	1550 ± 550	1590 ± 500
8	1080 ± 200	700 ± 150	450 ± 80
		620 ± 130	

<sup>a</sup>The root section, midsection, and distal section are approximately 2 to 6 cm, 6 to 15 cm, and 15 to 21 cm from the root, respectively.

#### Intensity of $\text{Hg}^{++}$ Absorption

In the next series of experiments, six hair samples were soaked for 140 h (that is, essentially to saturation) in tracer solutions of equal concentration. The solutions used were adjusted in pH to near 3, 5.5, and 8, and two hairs were soaked in each solution with a given pH value. It was found that hairs soaked at a pH near 3 absorbed the smallest amount of  $^{203}\text{Hg}^{++}$ , and those soaked at pH near 8 absorbed the largest amount. The relative intensities observed in the pattern near 10 cm from the root are shown in Table 3. This corresponds to the higher absorption capacity at large pH values for cations generally, as observed by Bate [10],

In a continuation of this experiment, the hair samples soaked at pH values near 3 and 8 were then soaked for an additional 144 h in the same solutions as used previously, but with the pH values reversed from those to which the hairs were first exposed. Typical results are shown in Figs. 9 to 11. From the experiments described above, the expectation is that a situation close to equilibrium between the hair shaft material and the surrounding solution is

TABLE 3—Relative intensities at 10 cm for hair shafts soaked at different pH.

pH 3	pH 5.5	pH 8
3.6	5.5	9.8
4.6	7.0	16.4

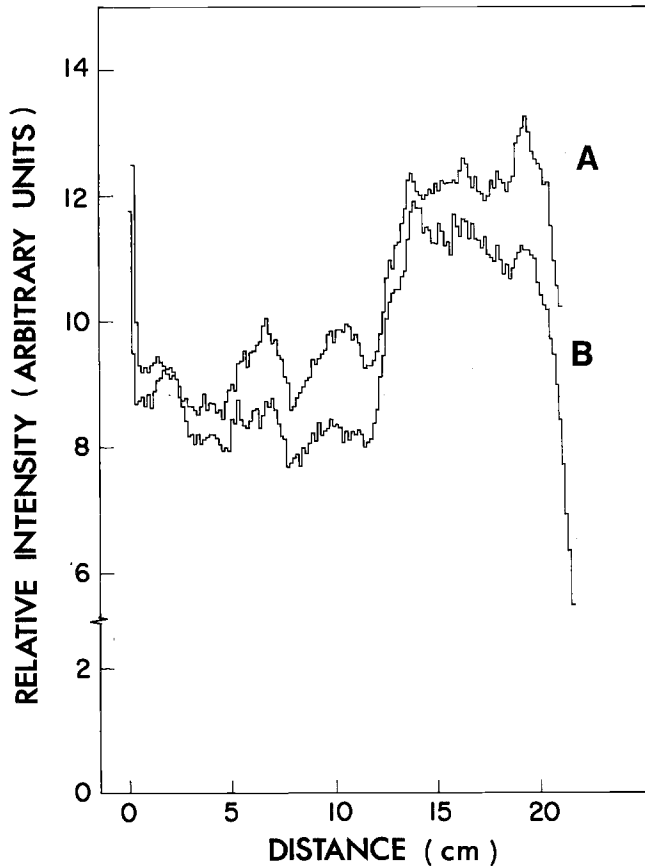


FIG. 9—Absorption of radioactive  $Hg^{++}$  by a single hair shaft as a function of distance from the root end following soaking to equilibrium in tracer solution initially at pH 8 (Curve A) and then at pH 3 (Curve B).

achieved in about 144 h; thus, a pattern change in the second of the soaking operations is expected, from that characteristic of the pH of the solution used in the first soaking to that characteristic of the one used in the second.

The observations confirmed the expectations. For example, a hair originally soaked at pH 8 shows a pattern intensity reduction when soaked at pH 3, corresponding to the lower equilibrium absorption of mercury tracer from solution at the new pH value. There is in these experiments, for the first time, evidence that the relative intensity of the pattern features changed with additional soakings, in this case in response to a pH change. Further, the most marked changes occurred towards the distal extremity of the hair shaft and are fur-

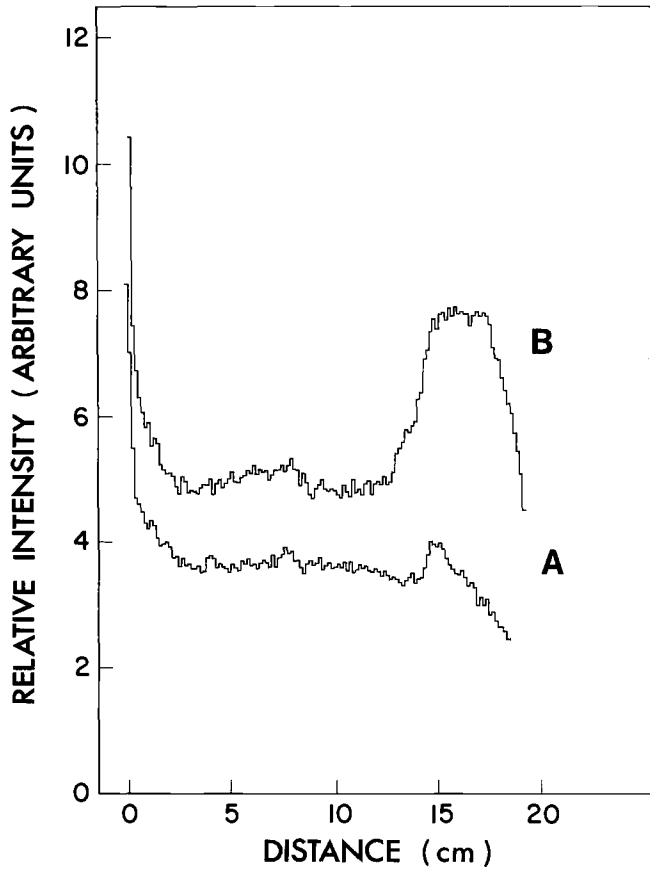


FIG. 10—Absorption of radioactive  $Hg^{++}$  by another single hair shaft as a function of distance from the root end following soaking to equilibrium in tracer solution initially at pH 3 (Curve A) and then at pH 8 (Curve B).

ther evidence (summarized below) of a change in the hair shaft chemistry with distance from the root. However, not all hairs showed this behavior to a comparable degree, and this is further evidence of the variability of the characteristics (observed earlier) among hairs drawn from a single human subject.

#### *Comparison of $Hg^{++}$ Absorption to $Cu^{++}$ and $I^-$ Absorption*

The absorption behavior of hair towards  $Hg^{++}$  ion was compared with that towards the  $Cu^{++}$  ion [1] examined earlier. Hair samples were soaked in 62-h  $^{67}Cu^{++}$  tracer solution of the concentration given earlier (for periods of 63 to 81 h), and the absorption patterns were measured as before. The samples were then set aside while the  $^{67}Cu$  activity decayed to negligible levels. Then a soaking in  $^{203}Hg^{++}$  solution was performed, with a total mercury concentration of 0.020 mg/mL, and the scanning repeated. The two sets of absorption patterns as shown in Figs. 12 and 13 were similar, with higher absorption of the cations at the distal end of the hair shaft. The  $^{67}Cu^{++}$  pattern was the more steeply sloped, with absorption of cation being slight at the proximal end and relatively intense at the extreme distal end of the hair shaft. Some localized areas of increased absorption were common to both the  $Hg^{++}$  and  $Cu^{++}$  patterns, but this was not true of all such regions that occurred.

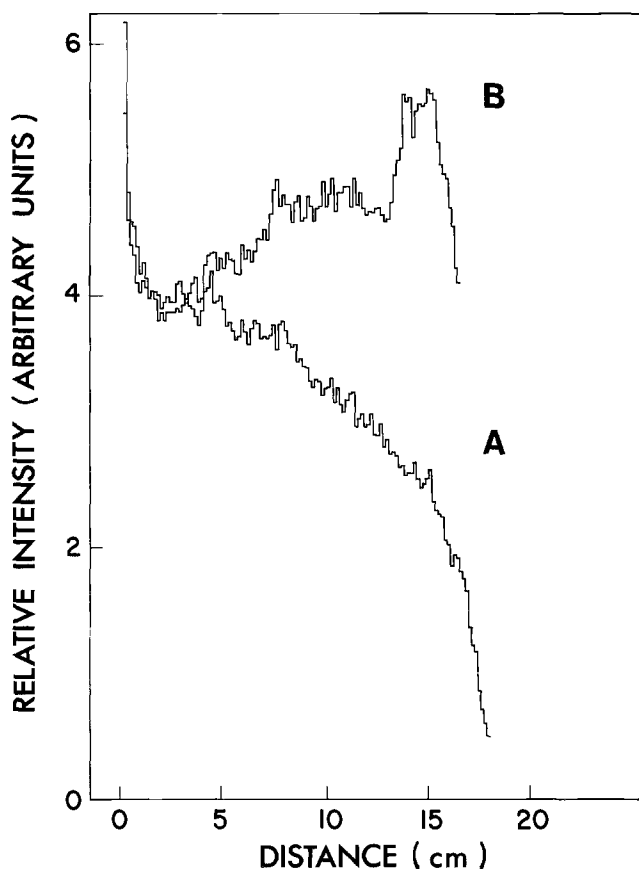


FIG. 11—Absorption of radioactive  $Hg^{++}$  by a third single hair shaft as a function of distance from the root end following soaking to equilibrium in tracer solution initially at pH 3 (Curve A) and then at pH 8 (Curve B).

Next, a comparison of the absorption of cationic  $Hg^{++}$  with that of anionic  $I^-$  was performed; quite different absorption patterns were expected from previous studies of  $PO_4^{--}$  uptake [4]. Hair samples were treated similarly to those in the above experiment, but 8-day  $^{131}I^-$  was used as the initial tracer and the soaking period was 37½ h. The general shape of the pattern of  $I^-$  uptake varied from one sample to the next, with a decrease in uptake with increasing distance from the root in one case but with absorption generally remaining constant in others. There appear to be more extreme local variations in the absorption intensity, with distinct  $I^-$  pattern peaks observed (see Figs. 14 and 15). The local areas of increased  $^{131}I^-$  absorption generally had a counterpart in the  $^{203}Hg^{++}$  pattern, but with different relative absorption intensity.

#### *Effect of Hair Bleaching*

Previous experiments [3] showed that severe cosmetic treatments, such as bleaching, resulted in a radically increased absorption, specifically of arsenate anion, in the bleached regions of the hair shaft. The availability of suitable hairs from a 56-year-old female prompted

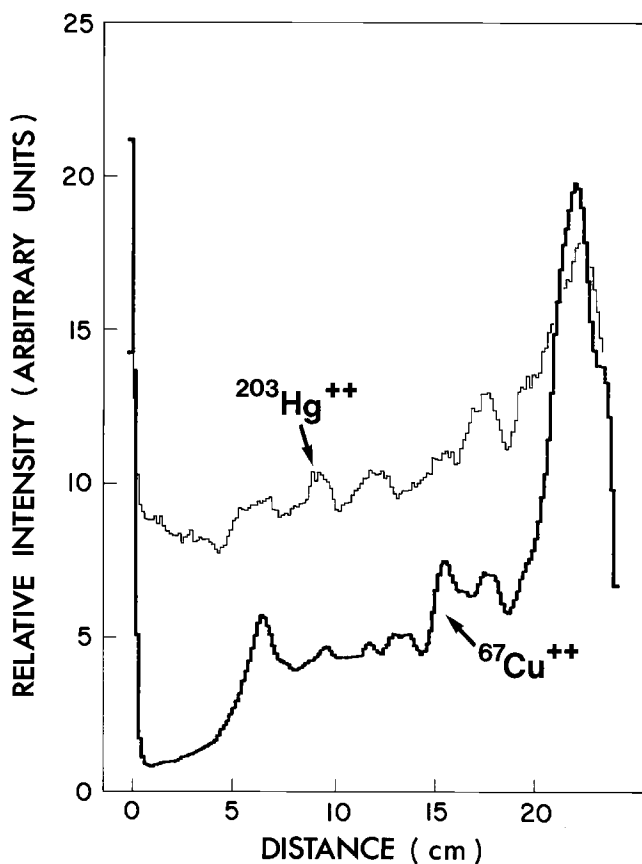


FIG. 12—Radioactivity intensity patterns observed in a single hair shaft following soaking in tracer solutions, first containing  $^{67}\text{Cu}^{++}$  and then  $^{203}\text{Hg}^{++}$ .

experiments to examine the corresponding phenomenon in the case of mercuric ion absorption.

The experiments were conducted only at a pH of 5.5 and with tracer solutions within the concentration ranges specified earlier. Soaking essentially to saturation produced the concentration patterns shown in Figs. 16 and 17. Regions of sharply increased absorption were observed to correspond in location with zones of bleaching along the hair shaft. Then experiments were conducted, similar to those described above, to measure the half-times for absorption and desorption of  $\text{Hg}^{++}$  from different regions of the hair shaft. The results are shown in Table 4.

### Discussion

The experiments reveal the influence of variations in the chemistry of the human head hair shaft on the uptake of mercuric ion from an aqueous environment. As such, they may assist the understanding of the origins of concentration variations along single hair shafts observed in subjects exposed to environmental mercury or to excess mercury from the diet subsequently applied externally to the hair shaft via sweat. They do not, of course, address

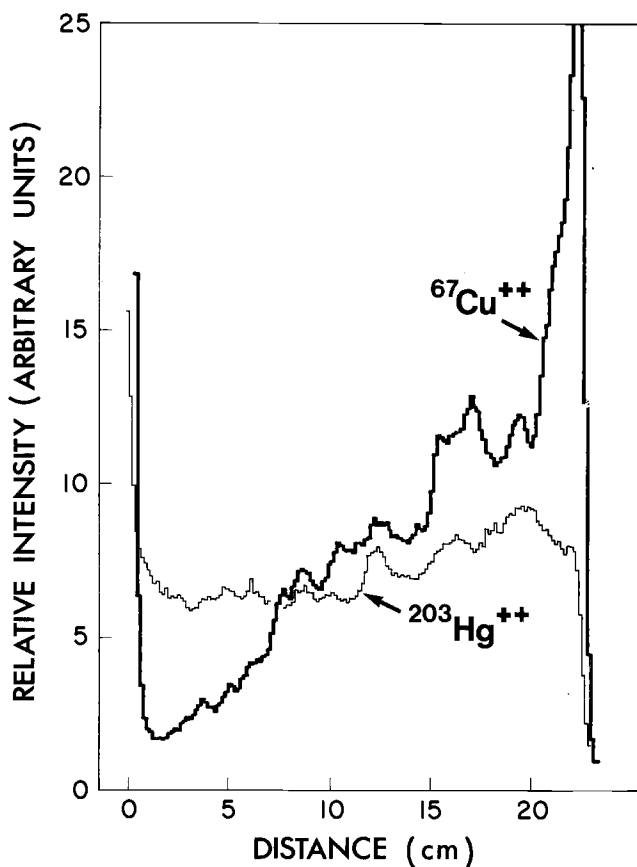


FIG. 13—Radioactivity intensity patterns observed in a second single hair shaft following soaking in tracer solutions, first containing  $^{67}\text{Cu}^{++}$  and then  $^{203}\text{Hg}^{++}$ .

variations arising from any direct incorporation of mercury into the growing hair shaft structure within the follicle.

The data show that the mercury concentration in hair shafts comes into equilibrium with the mercuric ion concentration of the surrounding aqueous medium in somewhat more than 100 h, with absorption of mercury being somewhat more rapid at low pH values and desorption more rapid at high pH values and towards the distal shaft extremity. (The pH range studied here extended from well above to well below that of the skin secretions and other aqueous media to which hair shafts are exposed.)

Presumably the rapidity with which the final concentration pattern is built up is controlled in part by the speed of diffusion of ions into the hair structure. Indeed, the existence of zones a few millimetres in length down the hair shaft, where higher mercury concentrations were observed than in adjacent regions, suggests that such regions support a higher diffusion rate than elsewhere. The fact that the relative intensity of peaks and other pattern features is maintained during the hundred and more hours of approach to equilibrium is consistent with this picture. So too is the existence of peaks in copper and iodine concentration patterns, which in many cases correspond in location to mercury concentration peaks in the same hair shaft. However, since the relative peak heights in, for example, copper patterns

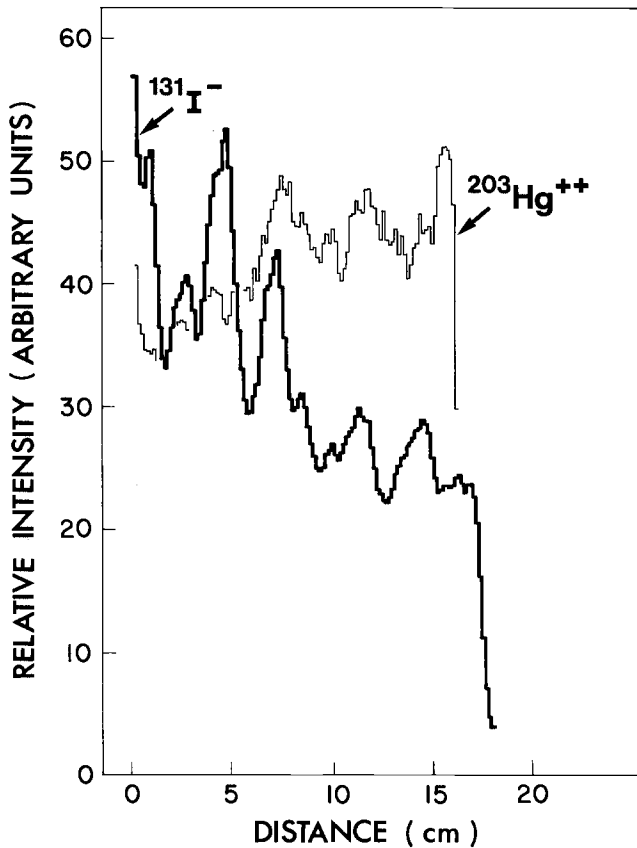


FIG. 14—Radioactivity intensity patterns observed in a single hair shaft following soaking in tracer solutions, first containing  $^{131}\text{I}^-$  and then  $^{203}\text{Hg}^{++}$ .

are generally different from those in mercury patterns, and since some peaks exist in one pattern without a corresponding peak in the other and pattern peak intensities change with changing solution pH values, diffusion is not the only influence at work.

An additional influence is also demonstrated by the data from experiments on bleached hair shafts. Table 4 indicates that  $\text{Hg}^{++}$  ions move somewhat less readily into and out of regions of the hair shaft that have been treated with bleaching agents. At the same time, Figs. 16 and 17 indicate that bleached regions do bind more mercury ions than adjacent nonbleached regions of a given shaft. Presumably the effect of bleaching is to create more mercury binding sites, which perhaps bind  $\text{Hg}^{++}$  ions more tightly and hence compensate for the effects on ion movement of the more open structure of bleached hair shafts, visible in scanning electron microscope images of them.

Another interesting (and similar) aspect of the data for normal (unbleached) hairs is the change in equilibrium concentrations with the distance from the root and with pH of the aqueous environment. At a given pH, typically three or four times more mercury is taken up by regions 15 to 20 cm from the root at equilibrium than by regions 2 to 6 cm from the root. This is a rather flat concentration gradient compared with those observed for copper absorption, for example, where the corresponding concentration ratio is nearer 20 or 30.



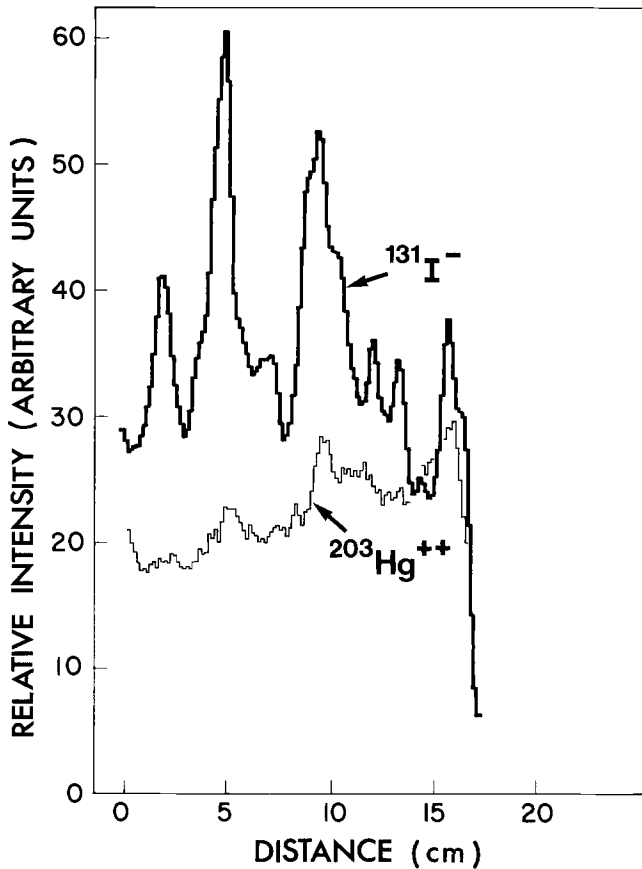


FIG. 15—Radioactivity intensity patterns observed in a second single hair shaft following soaking in tracer solutions, first containing  $^{131}\text{I}^-$  and then  $^{203}\text{Hg}^{++}$ .

Nonetheless, one would be tempted to ascribe the phenomenon to a distal hair structure progressively more porous, or otherwise more conducive to more rapid diffusion of mercury, copper, or other ions, were it not for the data on absorption of iodine and other anions. Generally, the absorbed concentrations of such species fall with increasing distance from the root.

Presumably, therefore, the sites in the hair structure to which ions bind include a greater proportion that bind cations and a smaller proportion that bind anions with increasing distance from the root. These proportions are also evidently affected by the pH of the surrounding solution, as seen from the data in Table 3. As much as three or four times more mercury is absorbed at equilibrium from solution at pH 8 than at pH 3. The data of Figs. 9 to 11 show that this is not just a change in the hair porosity (or some other physical factor) affecting diffusion rates. If the pH is changed from 8 to 3 and the hair again soaked to equilibrium, the mercury concentration reduces to the lower value characteristic of the lower pH.

The biggest changes of this latter kind occur away from the shaft regions adjacent to the hair root. This, coupled with the flatness of the mercury pattern (compared with the steep

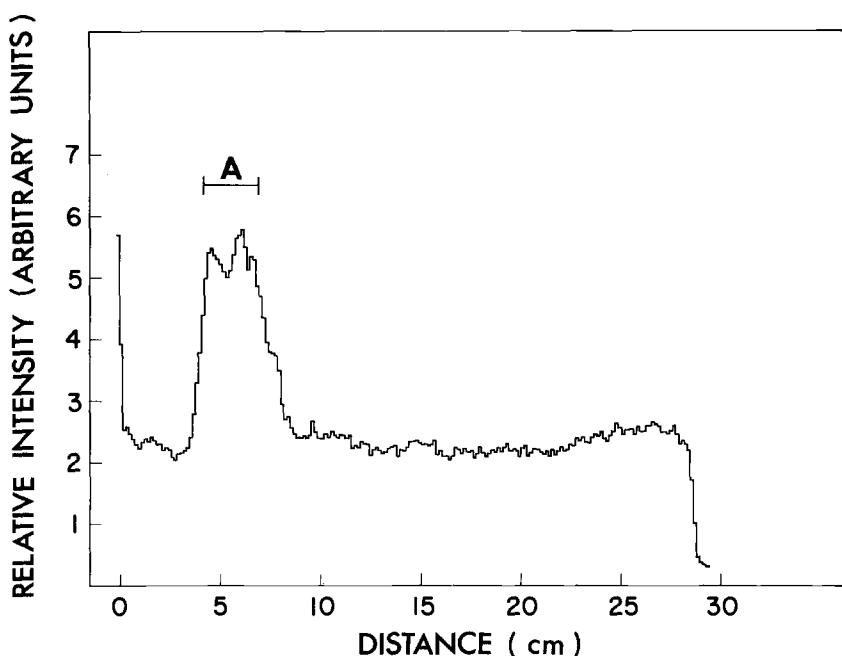


FIG. 16—Concentration pattern for  $^{203}\text{Hg}^{++}$  in a partly bleached single hair shaft following soaking to equilibrium. Region A of the hair shaft was bleached, while the remainder of the hair shaft was unbleached.

copper pattern), suggests that perhaps mercury binding is more complex than copper binding and that perhaps more than one kind of binding site is involved (for example,  $-\text{SH}$  and  $-\text{CO}_2\text{H}$  groups in the keratin structure). If so, the data, especially in Fig. 11, are consistent with a proportion of the different kinds of sites available for mercury binding being dependent on pH values. Furthermore, the data in Fig. 10 suggest that concentration pattern peaks may be due to more than locally enhanced diffusion. The large peak in the pattern of that figure was evidently largely due to an enhanced local concentration of binding sites, which were activated by a change from pH 3 to pH 8. To reveal the exact nature of these binding sites will take further, more sophisticated experiments.

### Summary

Individual hair shafts were exposed to aqueous solutions containing mercury (and copper and iodine) radiotracer, with a range of pH values. The concentration profiles along the hair shaft were then measured via radioactivity assay, as a function of the concentration and pH variables and of elapsed exposure time.

The results may be discussed in terms of the chemistry of the hair shaft in respect to binding metallic and nonmetallic ions. While diffusion rates for ions into the hair shaft show small general changes with distance from the root, and with the pH of the solution, the hair binding sites for cations evidently become generally more numerous towards the distal end of the shaft. However, with mercury binding there is evidence for more than one kind of binding site, and local maxima in absorbed mercury concentration are evidently due in large part to a higher local concentration of sites for cation binding.

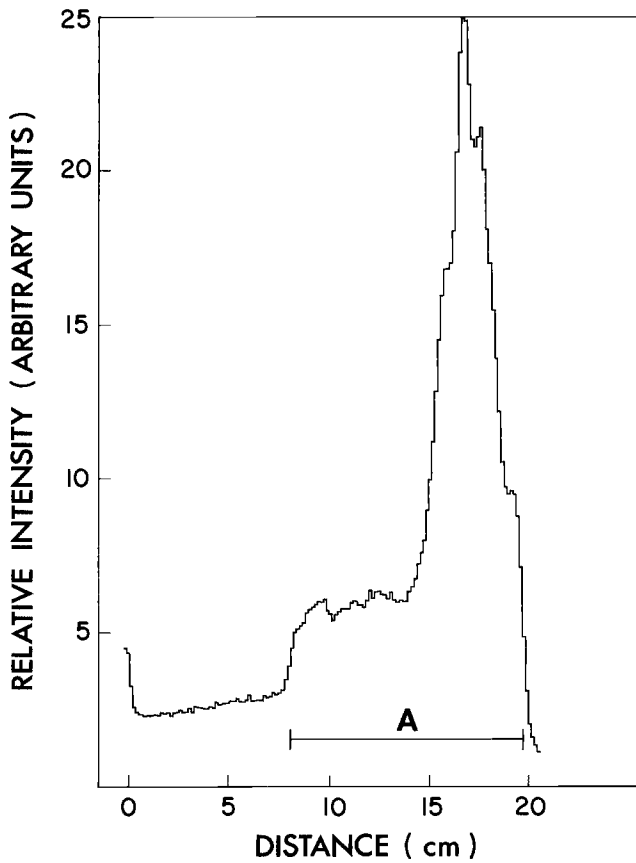


FIG. 17—Concentration pattern for  $^{203}\text{Hg}^{++}$  in a second bleached single hair shaft following soaking to equilibrium. Region A of the hair shaft was bleached, while the remainder of the hair shaft was unbleached.

TABLE 4—Half-times (hours) for absorption and desorption of  $^{203}\text{Hg}^{++}$  into bleached hair shaft regions compared with unbleached regions.

	Bleached	Unbleached
Absorption		
Hair 1	$37 \pm 1$	$37 \pm 1$
Hair 2	$158 \pm 10$	$90 \pm 12$
Desorption		
Hair 1	$500 \pm 300$	$380 \pm 135$
Hair 2	$650 \pm 345$	$315 \pm 95$

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