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FORENSIC APPLICATIONS OF TRACE ELEMENTS IN HAIR\*

CASH PRICE

L. C. Bate and F. F. Dyer

Analytical Chemistry Division  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee

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I. Introduction

The individualization of people by the trace elements in their hair appears to be probable on a laboratory scale when multiple hair strands are analyzed. The reasons for this technique showing promise are due to the following conditions: (1) a relatively large number of trace elements can be precisely measured, (2) all the hairs can be ascribed to their respective donors and therefore the hair-to-hair variability is made small, and (3) the conditions of the samples can be closely controlled to prevent contamination.

In most criminal cases, however, these conditions are not met and the practical application of the method continues to be seriously in doubt. To date, at least four criminal cases in which trace element comparisons were a part of the evidence have gone before United States courts. The evidence was accepted by the court in only one case. It remains to be seen if the three failures of this type of evidence to be legally acceptable will affect future cases.

II. Factors Affecting Identification

Barring the influence of contamination and changes with time after a sample of hair is removed from a person, the problem of matching a

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sample of hair to its donor is probabilistic in nature. The chance of making a correct match depends on (1) differences in trace element contents between persons, the between-persons variability and (2) the combined effects of variations in hairs from the same heads, the within-person variability, and experimental errors.

It is becoming increasingly clear that variations among hairs from the same heads are significant and may prohibit comparisons when only a few hairs are available. We have been asked to attempt comparisons in several criminal cases in which only one hair was found at the crime site. Our experience with single hairs indicate that the within-person variability is too large to permit one hair to be matched to a donor.

The reasons for hairs from the same head having different trace element concentrations have not been fully explained. The evidence obtained thus far indicates that adsorption of trace elements from environmental sources, e.g., water, perspiration, cosmetic agents, etc., is responsible for most of the trace elements in hair. It is known that hairs of widely different ages occur on a person's head<sup>(1)</sup> because some are growing and some are not. One would expect, therefore, that if environment adsorption is the primary source of trace elements, those of different ages and lengths as well as those in different positions would exhibit differences in concentrations.

Residues from dust, perspiration, cosmetics, and other material that are on the surface of the hair must be removed before the trace elements in the hair are measured. After a thorough study of cleaning hair by various methods<sup>(2,3)</sup>, it was concluded that the most desirable method to clean hair is with a non-ionic detergent—Kyro EO. This method compares

favorably with normal "in situ" washing of hair to remove surface contamination from the hair. The washing procedure consists of adding three drops Kyro EO to 20 ml redistilled water containing the hairs in a pre-cleaned plastic vial. The hairs are washed by shaking the vial for five minutes. The hairs are rinsed in redistilled water. This procedure is repeated two times with the washing time increased to 20 minutes instead of five minutes. Table I illustrates the amounts of the trace elements removed in each wash.

### III. Adsorption of Trace Elements in Hair

The belief that environmental adsorption alters the trace element composition of hair is based on the following observations.

- (1) The composition is altered drastically by the application of certain dyes and medicinal agents.
- (2) The concentration of most trace elements increases with distance from the scalp toward the outer ends.
- (3) Radioiodine given to thyroid patients is soon found strongly adsorbed in the outer parts of the patients' hair.
- (4) When hair samples are placed in aqueous solutions, almost all elements present will adsorb to an extent much greater than their respective concentrations found in untreated hair.

Results are shown in Figure 1 for trace elements measured in the hair of a small boy with a scalp disease. The abnormally high concentrations of several elements were undoubtedly caused by a salve used to treat the boy's head.

Analytical results are shown in Table II for sectioned portions of long strands of hair. The significant increase shown for trace element

concentrations with distance from the scalp has also been observed by others. (4,5)

Several hair samples were obtained from the nape of the necks of thyroid patients given  $^{131}\text{I}$  at the Oak Ridge Institute of Nuclear Studies. Soon after it was given, there was no evidence of  $^{131}\text{I}$  in the hair. Samples that were taken during the following four days contained an easily measurable and increasing amount of  $^{131}\text{I}$ . Duplicate samples taken from the patients contained significantly different amounts of  $^{131}\text{I}$ . These results indicate clearly that a trace element can be rapidly eliminated from the body in perspiration and adsorbed in hair. Differences between duplicates also indicate a source of hair-to-hair variation of trace elements. It was also shown that a part of the  $^{131}\text{I}$  was strongly attached to the hair by washing the samples with an aqueous solution of Kyro EO (a non-ionic detergent). The fractions remaining after washing are shown in Table III.

A simulated perspiration solution<sup>(6)</sup> was made and a radiotracer was added with a known amount of stable ion. The pH of the solution was controlled to be between 3 and 6 and the actual pH was recorded. A 100-mg hair sample was added, then shaken to ensure contact and allowed to remain in the solution overnight. Sixteen hours later the solution was removed and the hair rinsed with water. Radioactivity measurements were made after this water rinse and again after a Kyro EO-washing.<sup>(2)</sup> The results of these experiments measuring the amount of each element adsorbed\* on the hair is reported in Table IV.<sup>(7)</sup>

\* The term adsorption has been used to represent the attachment to hair of elements in environmental media. It is not known whether this process is one of adsorption or absorption (or both) according to the conventional definitions of these terms.

The data show (Fig. 3) that cation adsorption for an element increases as pH 7 is approached, while the amount of anion adsorption for an element decreases (Fig. 4).

The amounts of the element adsorbed by the hair depend on both the pH of the solution in contact with the hair and the particular element used.

#### IV. Methods of Comparing Analytical Results

The method used to compare the results of trace element measurements of hair is pertinent both to laboratory study and criminal cases including presentation in court. There has not been general agreement about this aspect of the problem.

Comparison of data in graphical form as gamma-ray spectra should be rejected because of its subjective nature. We believe that, for this method of hair comparison to be placed on an objective basis, the trace elements must be identified and measured quantitatively and these results compared.

Comparisons have been made of concentration or photopeak ratios. (5) If this procedure is used, one of the elements in the sample can serve as an internal standard. The small differences in exposure to neutron flux obtained for different samples might thus be minimized. If, however, reasonable care is taken, experimental errors can be reduced nearly to the limit set by counting statistics. It has been observed with samples of only a few hairs that the largest source of error is not experimental error but the within person variability. For such samples comparisons of ratios appears more to confuse than aid in matching hair samples. A further argument against the use of ratios is that they are not unique quantities as witnessed by the fact that 200:100 equals 2:1. On the

basis of ratios, therefore, two samples differing markedly in absolute concentrations might appear similar. It should also be recognized that if  $N$  elements are measured, only  $N-1$  ratios are independent and can be compared. Additional ratios are redundant.

The statistical method developed by J. B. Parker<sup>(8)</sup> for evaluating the probabilities of mistakes in hair comparisons seems to be the most useful one at present. The method takes into account between-person and within-person variances but not possible correlations among the elements. Results for all the elements measured are combined into a single criterion for evaluating the probability that two samples come from the same person and the fraction of the population that might show indistinguishable concentrations. With the exception of Coleman's study<sup>(8)</sup> in England and Wales, no representative sampling has been made to permit application of a statistical treatment. There is some doubt that the variations found by Coleman can be extrapolated to another geographical location. There is doubt also that a statistical statement can be made for a crime sample consisting on only one hair.

#### V. Recommendations Concerning Further Study of Hair Comparisons

Because the hairs found at a crime site cannot be a priori ascribed to the same person, it will be necessary in most instances to consider each one separately. Unless single hairs can be readily matched, there is little need for extensive sampling of the population to determine the number of people having similar trace element concentrations. We believe that a study of single hairs should be made by simulating criminal cases. This procedure would consist of the selection of 1 to 7 hairs per person from perhaps 10 persons. Duplicates would be taken in some of the cases from up

to three individuals. The person collecting the samples would give them to an activation analyst for analysis and matching. The analyst would analyze each hair singly and would not know which samples, if any, were duplicates. The analyst could make comparisons by the method of his choice (graphical, quantitative measurements including statistical analysis), but would report his findings only in terms of which samples match and which do not match. The frequency of successes and failures in comparing samples in a number of these cases would easily convince anyone of the value of trace element comparisons. Such experiments in which only one or two hairs were taken would be particularly instructive because they would correspond closely to real criminal cases. Experiments of this type would yield data amenable to statistical treatment (if the samples are representative of the population) and they heighten the interest of the investigator.

Duplicates in a simulated case made at ORNL could not be identified by means of the number of trace elements that matched. In fact, there were a number of erroneous selections. As a result of this study, we believe it is not advisable at the present time for criminal investigators to attempt comparisons of single hairs found at a crime site. If bundles of hair are found that can be a priori ascribed to one person, comparisons might be feasible. Care must be taken to avoid comparisons of hairs that may have been contaminated and to prevent the contamination of samples after they are collected. Solutions used to wash hairs before irradiation or mount hairs for other examinations must be shown to be free of elements that will absorb. The fact that hair absorbs elements from its environment will always make caution necessary in the criminal

case. If controlled laboratory study shows that single hairs can be matched, it would then be desirable to carefully study environmental effects in simulated criminal cases. Such a study might delineate the environmental conditions from which criminal investigators could safely take hairs for trace-element comparison.

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Table I. Trace Elements Removed by Kyro EO

<u>Sample</u>	<u>Wash</u>	<u>Trace Element Concentrations, <math>\mu\text{g/gm}</math></u>			
		<u>Mn</u>	<u>Na</u>	<u>Br</u>	<u>Cu</u>
A	1	0.35	259	6.8	3.6
	2	0.08	5	ND	ND
	3	0.04	ND	ND	ND
	4	ND	ND	ND	ND
B	1	0.83	738	11	2.5
	2	0.01	2	1.4	ND
	3	ND	ND	ND	ND
	4	ND	ND	ND	ND
C	1	0.81	560	11.3	29.5
	2	0.08	5	1.3	2.9
	3	ND	ND	0.9	ND
	4	ND	ND	ND	ND

ND = not detected

Table II. Trace Element Concentration Measured as a Function  
of Distance from Scalp in Female Hair

<u>Segment, cm</u>	<u>Trace Elements, <math>\mu\text{g/gm}</math></u>			
	<u>Zn</u>	<u>Hg</u>	<u>Au</u>	<u>Cu</u>
0-2	268	0.85	$10.7 \times 10^{-2}$	14.8
2-4	288	1.08	$3.4 \times 10^{-2}$	16.2
4-6	376	0.76	$6.4 \times 10^{-2}$	20.5
6-8	450	1.19	$7.4 \times 10^{-2}$	24.7
8-11	523	2.00	$15 \times 10^{-2}$	36.4

Table III.  $^{131}\text{I}$  Remaining on Hair after Kyro EO Washing

Person	1st Sample %	Time Sample Taken hrs	2nd Sample %	Time Sample Taken hrs
A	32.2	24	33.0	72
B	44.5	48	55.9	120
C	24.6	48	45.1	120
D	22.5	48	35.1	120
E	38.1	48	*	
F	42.0	48	*	
Ave	$34.0 \pm 11.5$		$42.3 \pm 13.6$	
* No sample taken				

Table IV. Concentration of Element Adsorbed on Hair

<u>Element</u>	<u>Element Concentration, <math>\mu\text{g/g Hair}</math></u>		
	<u>pH 3.5</u>	<u>pH 4.5</u>	<u>pH 5.5</u>
$\text{Au}^{+3}$	28000	27300	26200
$\text{Hg}^{+2}$	3300	5100	6600
$\text{Zn}^{+2}$	131	440	920
$\text{Ag}^{+1}$	420	520	640
$\text{Cu}^{+2}$	28	102	255
$\text{Fe}^{+3}$	21	40	120
$\text{Cr}^{+3}$	26	61	96
$\text{Co}^{+2}$	3.8	20	95
$\text{Cr}^{+6}$	15	41	88
$\text{Mn}^{+4}$	3.3	13.5	69
$\text{Se}^{+4}$	215	116	47
$\text{Cl}^{-1}$	400	132	35
$\text{Ba}^{+2}$	2.1	8.0	25
$\text{Br}^{-1}$	158	66	20
$\text{I}^{-1}$	85	31	10
$\text{Sr}^{+2}$	0.72	2.7	9.8
$\text{Ca}^{+2}$	0.37	1.5	8.0
$\text{Sb}^{+5}$	8.8	4.5	2.7
$\text{P}$ (as $\text{PO}_4^{-3}$ )	6.1	2.0	1.66
$\text{As}^{+3}$	0.51	0.58	0.76
$\text{As}^{+5}$	4.2	1.7	0.66
$\text{Na}^{+1}$	0	0	0
$\text{K}^{+1}$	0	0	0
$\text{Cs}^{+1}$	0	0	0







