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The DS Method for Evidence Characterization

The scientific comparison of materials is often used as an aid to assigning responsibility for infractions of the law. A suspect, for example, may (or may not) be linked to the scene of a crime, depending on whether his hair matches (or does not match) hair found at the scene. The confidence in conclusions reached by such comparisons depends on the number of measured characteristics and the manner in which such characteristics vary among both the universe of such material and the appropriate subset; for example, the variance of hair among humans and the variance of hair on a single human.

It must be emphasized that matching characteristics between two samples is meaningless without a reliable estimate of the chance that the characteristics of the first sample may be matched by a random sample from the relevant population of samples.

Neutron activation analysis (NAA) has been used to compare many evidence samples because it accurately observes many points of comparison. The method is a very powerful technique for elemental analysis, and measures concentrations of a large number of trace elements (and major elements) in both natural and manufactured materials. Samples may be compared with respect to their elemental composition, where each element observed and its concentration in one sample is considered a point of comparison with respect to the other sample. Such points of comparison often outnumber the points of comparison used in fingerprint identification, and for this reason the combination of elements and their concentrations in a sample is sometimes called its "fingerprint"; however, we prefer the term "trace element pattern" (TEP).

Extensive studies of hair, paint, paper, and petroleum have been carried out, using NAA, to ascertain the usefulness with which TEP pairs can be compared for like materials, and a variety of mathematical methods for generating decision probabilities have been used to interpret the results.

In one study of over 1100 hair samples from 750 different persons, the concentration frequency distributions for 20 elements were obtained and the probability, P, of obtaining a given TEP was computed from $P = p_1 p_2 p_3 \cdots p_n$, where p_1, p_2, p_3, $\cdots$, and p_n are the respective probabilities that the observed concentrations of each of the n observed elements can occur [1,2]. Thus, given the TEP of one hair, it was assumed that P represented the chance that a random hair from the population would have a like TEP.

In another similar study of hair, concentration distributions obtained from hair of over 800 donors were treated with Gaussian statistics [3]. An envelope of TEP values representing 99 percent of head hairs from an individual was defined, and it was as-

sumed that a random hair from the population matched hair from the individual only if its TEP fell within the envelope.

In studies of 155 different paints [4] and 40 different white bond papers [5], simple probability products, $P = p_1 p_2 \ldots p_n$, (as in the first hair study cited) were used.

In the examination of nearly 300 samples of petroleum products (crude oil, residual oil, and distillates) from the population of U.S. continental maritime oil slicks, it was found desirable to develop a new statistical approach [6]. Non-Gaussian distributions of concentrations for many elements prevented the use of multivariate normal statistics, such as proved useful in the second hair study cited. At the same time, it was felt that the probability product approach did not adequately compare both the probability that two samples were matched and the probability that they were not matched. The new approach was called the Difference Score (DS) method, and enabled the computation of both probabilities.

The DS method is simple to apply, and enables a decision to be reached based on the probabilities of each of the two choices—"matched" and "not matched"—with regard to sample pairs. Therefore, the application of the method to hair, paint, and paper identification has been examined and the results presented herein. For completeness, relevant aspects of oil identification by the DS method are included.

The DS Method

Application of the DS method requires that both a representation of the population and replicate samples from individual sources within the population be obtained. The latter are used to define the variation of TEPs within individual sources. Such variation is comprised of random fluctuations within the source and random measurement errors; therefore, the individual source variation may be treated with Gaussian statistics. In practice, intrasource variance usually dominates measurement errors.

Given a sufficiency of replicates from a sufficiency of individual sources, the variation of individual elements may be described by the root mean square standard deviation, s_r.

$$s_r = \left[\frac{\sum\limits_{i=1}^{n} (s_i{}^2)}{n} \right]^{1/2} \tag{1}$$

where s_i is the standard deviation of an element among replicates for each of the n source samples.

As will be seen, the value of s_r is used to define numbered concentration increments for each element, which are used in turn to compute difference scores between sample pairs. Also, it will be shown that a priori estimates of difference score distributions from matched samples can be developed.

Bin Coding of TEPs

In the DS method the observed concentration of an element is expressed as a bin number, where the bin encompasses a range of concentrations. Bins are numbered sequentially from the lowest observable concentrations. The value of s_r for that element from population replicates is used to define the bin width, and the same multiple of s_r is used to define bin widths for each element that is to be used as a point of comparison. In this fashion all points of comparison are equally weighted.

Suppose, for example, Element A and Element B have s_r values of ±19 percent relative and ±38 percent relative, respectively, and it is decided to use $3s_r$-wide bins. Where the lower edge of a bin for Element A is at unity, the upper edge is at $1 + (3)(0.19)$, or 1.57, which is about $10^{1/5}$. Similarly, where the lower edge of a bin for Element B is at unity, the upper edge is at $1 + (3)(0.38)$, or 2.14, which is about $10^{1/3}$. Then each decade of concentration range may be divided into five bins for Element A and three bins for Element B. In the concentration range from 10 to 100 ppb (parts per billion parts by weight), for example, the sequence of bins for Element A would be Bin 1, 10 to 15.8 ppb; Bin 2, 15.8 to 25.2 ppb; Bin 3, 25.2 to 39.8 ppb; Bin 4, 39.8 to 63.1 ppb; and Bin 5, 63.1 to 100 ppb. For Element B the bins would be Bin 1, 10 to 21.5 ppb; Bin 2, 21.5 to 46.5 ppb; and Bin 3, 46.5 to 100 ppb. Then, if the concentrations of A and B in a sample were 70 and 15 ppb, respectively, their bin code numbers would be 5 and 1.

It may be noted that the logarithms of ppb concentrations for the given bin boundaries of A are 1.0-1.2-1.4-1.6-1.8-2.0, and for B are 1.000-1.333-1.667-2.000. In effect, the bin widths for an element are constant when concentration is expressed as the logarithm.

Computing the DS Value

Given bin code numbers n_i and m_i for the ith element in two samples, $|n_i - m_i|$ is a single measure of the difference between the two samples. For all k elements observed in both samples,

$$\sum_{i=1}^{k} |n_i - m_i|$$

is a more complete description of the difference.

Of course, in the event that a particular element is observed in only one of a pair of samples, a strong difference between the samples is implied. The difference between the measured value and the upper limit value in the respective samples may not be a true measure of the difference between unmatched pairs for that element; also, there is some chance that intrasource variance or an experimental anomaly can cause this to happen with matched pairs. For these reasons it was decided to simply add 5 to the difference score whenever an element was singularly observed. The effect of this arbitrary constant is adequately incorporated in the DS distributions for matched and unmatched samples to be described later.

The complete difference score, DS, is described by:

$$DS = 5j + \sum_{i=1}^{k} |n_i - m_i| \qquad (2)$$

where j is the number of elements observed in only one of a pair of samples.

Expected DS Distributions Among Matched Samples

Inasmuch as the total concentration range for a trace element covers several orders of magnitude in either natural or manufactured products (as will be seen later), and there are several concentration bins per order of magnitude, it may be assumed that there is an essentially linear probability of the true value of an element being at any point across its true bin. However, the probable difference between the true value and the experi-

mentally measured value will be in accord with the normal curve of error, and there is a chance that the observed value will fall in the adjacent bin, which is dependent on how close the true value is to the bin boundary and, also, on the bin width. Provided the bins are $\geqslant 2s_r$ in width, there is very little chance that the observed value will be two bins removed from the true bin.

Averaging the probabilities, b_i, that the observed values will fall in the true bin for true values across the bin gives a parabolic relationship between the bin width, w, and the chance, $\bar{b}$, that the observed value will be in the true bin.

$$\bar{c} = (1 - \bar{b}) = 0.78w^{-1} \tag{3}$$

where w is in s_r units and $\bar{c}$ is the chance that the observed value will fall outside of the true bin. Examples of the relationship are as follows:

w	$\bar{b}$	$\bar{c}$	w	$\bar{b}$	$\bar{c}$
2	0.61	0.39	6	0.87	0.13
3	0.74	0.26	7	0.89	0.11
4	0.80	0.20	8	0.90	0.10
5	0.84	0.16	9	0.91	0.09

Given a measured element in replicate samples of a given material: (1) both observed values will fall in the true bin or (2) one value will be in the true bin and one in an adjacent bin or (3) both values will be in the same adjacent bin. Since the chance of the latter becomes greater as the true value approaches the bin boundary, there is little likelihood that the two observed values will be on opposite sides of the true bin (<1 percent for $w = 3s_r$). The three dominant possibilities will follow the binomial distribution:

$$1 = (b + c)^2 \tag{4}$$

Thus, for $w = 3s_r$, $b = 0.74$, and $c = 0.26$:

(1) with both in the true bin ($n_i - m_i = 0$), $b^2 = (0.74)^2 = 0.5476$;

(2) with one in the true bin and one in the adjacent bin ($n_i - m_i = 1$), $2bc = 2(0.74)(0.26) = 0.3848$; and

(3) with both in the adjacent bin ($n_i - m_i = 0$), $c^2 = (0.26)^2 = 0.0676$.

Consider, for the moment, that there is no chance of failure to observe an observable element. The chance per element, p, that $n_i - m_i = 0$ is $b^2 + c^2$, while the chance per element, q, that $n_i - m_i = 1$ is $2bc$. Given n elements, the probabilities for DS = 0, 1, 2, ... n will be described by representative terms of the binomial $(p + q)^n$; namely:

$$DS_i = \binom{n}{i} p^{n-i} q^i \tag{5}$$

For example, given $w = 3s_r$ and ten elements, $p = 0.6152$ and $q = 0.3848$ and DS = 0, 1, 2, ... 10 are, respectively, 0.00777, 0.0486, 0.137, 0.228, 0.250, 0.187, 0.0976, 0.0350, 0.00819, 0.00114, and 0.000071, for the case of no observable elements missed.

It is found from experimental data on matched pairs that there is a chance, u, that an observable element will be observed in both samples of a pair of samples, and a chance, v, that the element will be observed in only one of the samples. Given n elements, the

number of observable elements that will be seen only once in a matched pair of samples, O_j, is given by:

$$O_j = \binom{n}{j} u^{n-j} v^j \qquad (6)$$

If one observable element is seen only once, five units are added to the difference score. The remaining $(n-1)$ elements follow Eq 5 for DS values of 5, 6, 7, . . . $(n + 4)$. If two observable elements are missed, Eq 5 applies for the remaining $(n-2)$ elements for DS = 10, 11, 12, . . . $(n + 8)$.

A significant chance of missing three observable elements once in a matched pair occurs with paper, but has not been found for any other combination of material and procedure treated in this study. Thus, the distribution of DS_i, for $i = 0, 1, 2. . . (n + 12)$ is given by the summation of the terms:

$$DS_i = \sum \begin{cases} o_0 \binom{n}{i} p^{n-i} q^i, & i = 0 \text{ to } n \\[2em] o_1 \binom{n-1}{i-5} p^{n+4-i} q^{i-5}, & i = 5 \text{ to } (n + 4) \\[2em] o_2 \binom{n-2}{i-10} p^{n+8-i} q^{i-10}, & i = 10 \text{ to } (n + 8) \\[2em] o_3 \binom{n-3}{i-15} p^{n+12-i} q^{i-15}, & i = 15 \text{ to } (n + 12) \end{cases} \qquad (7)$$

Observed DS Values

The samples collected from the populations of hair, oil, paint, and paper measured by NAA included both numerous different samples and a number of replicates of given samples. Pairs formed from different samples (for example, paint from two different automobiles or head hair from two different individuals) are classified as unmatched pairs, while replicates (for example, two paint samples from a given automobile fender or two hair samples from an individual's head) are classified as matched pairs.

It is necessary to further distinguish between loosely and closely matched pairs. For example, because TEPs of head hair are not constant with time, hairs obtained from an individual's head several months apart are more loosely matched than those obtained simultaneously. Similarly, two paint samples from a given fender tend to be more closely matched than a pair comprised of samples from a fender and hood of the same automobile, since the parts may be painted separately. Further examples may be found in Refs 2 and 4-6.

Data presented in Refs 2 and 4-6 have been taken for conversion to DS scores in accordance with the method described by Eq 2. All samples from a population were not necessarily paired with all others of that population. A maximum of 90 samples could be handled as a set by the computer program, so that 720 different hair samples were processed by computing all DS scores within each of eight groups of 90 samples. Pairings of different oil samples were done on a regional basis (West, Gulf, and East Coasts), while paints were paired only within color classifications. Only in the case of

TABLE 1—*Bin coding base on closely matched samples.*

Bins per Decade of Concentration	Hair		Oil		Paint		Paper	
	Elements[a]	s_r, % relative	Elements[a]	s_r, % relative	Elements[a]	s_r, % relative	Elements[a]	s_r, % relative
2	Br	70	Al, Zn, Na, Dy	74	Zn	62	Cr, Sb	68
3	Ni, Se, Sb, Hg	37	Ni, I, Ga, As, Co, Cl	40	Ba, K, W	33	Ti, Mn, Na, Cl	36
4	Fe, Cu, Ga, As, Au	25	Br, Mn, Ba	27	Mn, Na, Ca	22	Al, Ca	24
5	Na, Zn, Ag, La	18.7	S, In	20	Br, Cl, Sb	17	Zn	18
6	Sr	15.2			Ti, Co, Ta	13		
7	Mn, Rb, Cs	12.6			Al	11		
8	Cr	10.6			Cr	9		
10	Co	6.7	V	9				
Bin Widths, s_r, units	3.1		2.9		3.5		3.2	

[a] Only those elements observed with sufficient frequency to provide a good estimate of s_r in replicates used.

bond paper were the different samples all paired with one another. Values of s_r and the number of bins used per decade of concentration are given for each frequently observed element in Table 1. Relevant information associated with the DS scoring of the sample sets is given in Table 2.

TABLE 2—*Information regarding DS scoring of TEP data.*

	Evidence Material			
	Head Hair	Oil Slicks	Paint	Paper
A. Number of Sample Pairs				
1. unmatched samples	32 040	6997	3073	780
2. loosely matched samples	1 236		92	157
3. closely matched samples	63	24[a]	22	20
B. Number of Elements				
1. observed among all samples	20	35	37	10
2. maximum observed within one sample	20	20	25	9
3. in statistical base[b]	20	16	15	9
4. average number observed within statistical base	14	10	11	6
C. Codification and Theoretical DS Values for Replicates				
1. bin widths, s_r units	3.1	2.9	3.5	3.2
2. b (see Eq 3)	0.746	0.724	0.770	0.747
3. p	0.621	0.607	0.646	0.622
4. v	0.02	0.013	0.035	0.105
D. Average Elemental Concentration Range, bins/element	14.5	14.9	16.8	6
E. Average DS Value for Unmatched Pairs	55	54	47	21

[a] Replicates of oil-slick samples no more than four miles or seven days apart.
[b] See Table 1.

From values for the C items in Table 2, the theoretical distribution of DS scores for replicates, where average n (see Table 2, B4) is used, was computed for each material. These are lumped and given in Table 3, together with observed distributions for both matched and unmatched pairs.

Discussion and Conclusion

The distributions of DS values given in Table 3 are usefully different for closely matched and unmatched pairs of hair, oil, and paint. Specifically, for these materials the following statement can be made at the > 99-percent level of confidence: if DS ≤ 16, the sample pair is matched. At the same high level of confidence it can be said that if DS ≥ 17, either the sample pair is unmatched or loosely matched. In any event, if DS ≥ 17, it cannot be stated with confidence that a suspect sample matches an evidence sample.

Inasmuch as 6.28 percent of unmatched paper pairs have DS ≤ 8, no definitive identifications of matched pairs of paper appear possible at this time. However, it may be noted that current NAA techniques could easily obtain TEPs from paper with an average of more than six elements. Hence, an updated study of paper could provide the basis for definitive statements regarding this material.

The DS probabilities for a matched pair with a number of elements other than the

TABLE 3—DS distributions, observed and theoretical, %

DS Value	Hair Unmatched Pairs	Hair Matched Pairs			Oil Unmatched Pairs	Oil Matched Pairs		Paint Unmatched Pairs	Paint Matched Pairs			Paper Unmatched Pairs	Paper Matched Pairs		
		Loose	Close	Theory[a]		Close	Theory[b]		Loose	Close	Theory[c]		Loose	Close	Theory[d]
0-8	0.025	16.4	76.1	76.7	0.00	91.6	93.2	0.065	55.5	68.2	79.7	6.28	72.9	90	85.8
9-16	0.231	12.2	23.9	23.3	0.857	8.4	6.8	0.521	24.0	31.8	20.3	19.87	26.0	5	13.2
17-24	1.17	15.7			4.60			3.32	18.5		0.06	39.87	1.1	5	0.5
25-32	3.24	18.6			9.90			9.31	2.0			22.95			
33-40	6.77	6.7			15.78			18.71				10.39			
41-48	14.85	13.8			17.58			24.50				0.64			
49-56	24.37				15.62			19.79							
57-64	24.93				11.64			13.02							
65-72	16.02				8.82			6.54							
73-80	6.24				6.23			2.54							
81-88	1.74				3.81			1.37							
89-96	0.350				2.73			0.305							
97-104	0.056				1.64										
105-112	0.003				0.729										
113-120	0				0.057										

[a] 14 elements.
[b] 10 elements.
[c] 11 elements.
[d] 6 elements.

average (see footnotes in Table 3) can be computed from Eq 7. These may be compared with the DS distributions of unmatched pairs, given below in greater detail.

DS Value	Hair, %	Oil, %	Paint, %
0-4	0	0	0
5-8	0.0125	0	0.065
9-12	0.050	0.214	0.163
13-16	0.181	0.643	0.358
17-20	0.387	1.70	1.17

The studies [2,4-6] from which the DS distributions have been obtained involved loosely matched pairs of samples in an exploratory sense; for example, it was necessary to define the possibility of using hair taken months after a crime or paint from adjacent parts of a car, refrigerator, etc. It is clear from these works that care is required in obtaining suspect and evidence samples. That is, if a door has been jimmied, it will be necessary to sample paint from both the door and the doorjamb for comparison with paint flecks obtained on suspects' tools. Allowance for a growth rate of 1 cm per month enables one to estimate the fraction of a hair sample that has grown since the time of a crime. Data are currently lacking for the integrity of oil spills after seven days of weathering. These and other constraints associated with closely matching pairs may be obtained from the studies cited. Where significantly correlated elements are included in DS scores, one must expect smaller scores than if no such correlations existed. If too many such elements are involved, the spread of DS scores would not be useful. Clearly this has not happened in the present studies of hair, oil, and paint.

Given that samples are obtained under conditions that avoid loose matching, it is concluded that evidence and suspect samples of hair, oil, or paint may be shown to match or not match with a high degree of confidence by the DS method of interpreting TEPs obtained by NAA. Furthermore, since the application of the DS method to these different materials indicates a generality of application, it is likely that the method would prove applicable to other kinds of evidence materials where numerous points of comparison may be made, provided the proper statistical foundation is obtained by population sampling (with replicates) and analysis.

Summary

Neutron activation analysis (NAA) has been shown to be a useful method of evidence characterization via the trace element patterns (TEPs) of evidence materials. Comparison of an evidence sample TEP with the TEP of an appropriate sample obtained from a suspect provides an indication as to whether the suspect can or cannot be linked to the crime depending on whether the two samples' TEPs are matched or not matched. This paper described an objective scoring method, the Difference Score (DS) method for comparing TEPs, and its application to samples of hair, paint, oil, and paper. The necessity for an adequate data base from the population of material is described.

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