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Differentiation of Bullets by Spark Source Mass Spectrometry

Matching of evidence bullets with a particular suspect is most frequently accomplished by comparing the striations on the evidence bullets with those on test bullets fired from the suspect's gun. This method cannot be used, of course, when the striations are obliterated or when the gun is not available for test-firing. In this case, if unspent bullets are found in possession of the suspect, they may be chemically compared with the evidence bullets. Identical elemental composition is usually taken as evidence that the bullets may have the same origin; that is, they may have come from the same box or lot.

The most comprehensive forensic study of elemental composition of bullets was done by Lukens et al [1], employing instrumental neutron activation analysis (NAA) to determine antimony (Sb), copper (Cu), and arsenic (As). Using these three elements they were able to distinguish less than half of the 75 lots of bullets examined. Brunelle et al [2] examined a large number of .38-caliber bullets from three major manufacturers using the atomic absorption method. They showed that there are significant batch-to-batch variations in concentrations of Sb, Cu, silver (Ag), and bismuth (Bi). Both of these studies emphasized the need for a method of determining more elements. Accordingly, Guy and Pate (3) attempted radiochemical separation of the interfering Sb after neutron activation of bullet lead. The technique was only partially successful, allowing quantitative determination of four to seven elements.

Spark source mass spectrometry (SSMS) offers virtually complete elemental coverage with high sensitivity. Therefore, it is potentially the best method for characterizing any substance according to its elemental composition. This study will demonstrate the application of SSMS to the bullet identification problem.

A complete study of this sort should be based upon a statistically random sampling of the bullet population. The data could then be used to estimate the probability of a given "match" occurring. Such studies have been done on window glass in Britain [4] and on paints in the United States [5], using neutron activation analysis. This paper instead will pursue the more modest goal of quantitatively estimating the "similarity" of bullets [6]. For comparative purposes, both SSMS and instrumental NAA will be used.

Therefore, the boxes of bullets to be analyzed were not randomly selected, but were chosen so as to provide a fair test of the abilities of the methods to distinguish bullets. Ten boxes of .38 Special revolver bullets were analyzed. Five of these were Winchester,

of various known dates of manufacture. The other five consisted of one box each from Browning, Federal, Remington, Smith & Wesson (S&W), and Speer.

Experimental

The mass spectrometer was the Model MS702 manufactured by Associated Electrical Industries, Ltd. It is equipped for electrical detection; however, the more conventional photoplate detection method was used throughout this study. A detailed description of the analysis method is given in a companion paper [7].

Electrodes were cut from the bullet to dimensions of approximately ½ by 1 by 4 mm. Since plenty of sample was available in this study, larger electrodes than necessary were used. Only about 10 mg of lead (Pb) are actually consumed during analysis and 15 to 20 mg would therefore be the minimum sample size required for complete elemental analysis down to the 0.1 ppm level and below. Samples smaller than this could be analyzed, but with a proportionate decrease in sensitivity.

In order to obtain accurate concentrations with SSMS, a standard sample of the same matrix must be analyzed under identical conditions. The only standards available which approximate bullet lead composition are the Kirk leads A626 and 604 (Morris P. Kirk and Sons, Los Angeles, Calif.). However, both of these standards together only have six elements (Cu, As, Ag, Sn, Sb, and Bi) of certified concentrations. Therefore, all other elements can only be determined in a relative sense. It has been found that values determined this way are usually within a factor of three of the correct concentrations [8]. Note that for comparative purposes, however, it is precision instead of accuracy that is required.

The samples were also analyzed in this laboratory by instrumental NAA for Sb, Cu, and in some cases As. The procedure is conventional and will not be elaborated here. See Ref 1 for a general description of the method.

Results and Discussion

Suitable Elements

The elements commonly found in the bullets studied here are listed in Table 1. Sulfur (S) and most of the heavier elements, from Cu to Bi, are qualitatively characteristic of the lead matrix. That is, these elements form an easily recognized pattern by which the matrix may be identified, even without observation of the matrix lines of the mass spectrum. The lighter elements, with the exception of S, occur at levels that might be found in almost any matrix and cannot be considered qualitatively characteristic. Nevertheless, we will take the approach that all elements are of equal value a priori.

SSMS is remarkably free of interelement interferences. Of the 26 elements in Table 1, only four have any significant interference problems. These elements, and the interfering species, are $Si(Fe^{+2})$, $Cr(Pb^{+4})$, $Mn(Cd^{+2})$, and $Ni(Sn^{+2})$. Even these elements can be determined in certain samples where the interfering species are present at low concentrations.

Sodium (Na), titanium (Ti), iron (Fe), and zinc (Zn) were observed to be distributed very inhomogeneously in the bullet lead samples. This is manifested by widely fluctuating apparent concentrations of these elements on the different photoplate exposures. The resulting uncertainty in the bulk concentrations makes these elements unsuitable for quantitative analysis.

Another criterion for establishing suitable elements is uniformity over the bullet as a

TABLE 1—*Elements commonly found in bullet lead.*

Element	Concentration Range, ppm	Occurrence, %	Element	Concentration Range, ppm	Occurrence, %
B	0.01–0.3	75	Ni	0.1–5	30
Na	1–10	100	Cu	10–1000	100
Al	0.1–10	100	Zn	0.1–10	90
Si	0.1–3	100	As	1–1000	100
P	0.01–0.1	80	Se	0.1–10	50
S	1–300	100	Ag	5–75	100
Cl	1–10	100	Cd	0.1–10	75
K	1–10	100	Sn	1–6000	50
Ca	1–10	100	Sb[a]	0.4–5	100
Ti	0.1–3	30	Te	1–50	100
Cr	0.1–1	50	Hg	0.1–50	20
Mn	0.1–1	75	Tl	0.1–10	100
Fe	1–100	100	Bi	5–500	100

[a] Percent.

whole. Table 2 shows the results of analysis of three different sections of a single bullet. Aluminum (Al), chlorine (Cl), potassium (K), and calcium (Ca) have much higher concentrations in one section than in the others. In general, these elements did not have very reproducible values on rerun analyses of the same bullet. These are elements that one might expect to find in inclusions of dirt or slag incorporated in the lead during smelting. Regardless of the source, the nonuniformity of these elements over the bullet makes them less desirable for characterization purposes.

Thus, 12 of the 26 elements in Table 1 are rejected for general characterization studies because of interference or homogeneity problems. (Nonuniformity is actually inhomogeneity on a larger scale.) In addition, boron (B) and phosphorus (P) will be rejected because they are found only at very low levels, usually less than 0.1 ppm. This leaves S, Cu, As, selenium (Se), Ag, cadmium (Cd), tin (Sn), Sb, tellurium (Te), mercury (Hg), thallium (Tl), and Bi as elements suitable for quantitative study. Note that these are the "characteristic" elements mentioned above.

Precision

The average relative standard deviation (RSD) in Table 2 is 19%. This figure is typical of the precision of replicate analyses of bullets by this method. Table 3 shows the results of replicate analyses of the Kirk lead standards A626 and 604. The average RSD of the two runs on A626 is 9% and the agreement of the calculated relative sensitivity factors between A626 and 604 is at least this good. The degradation of precision found for bullets is mostly attributable to inhomogeneity, a common problem in bulk analysis of real samples by a sensitive technique such as SSMS. Although the experimental precision of the method is probably less than the inherent variation for many elements, a more precise method is still desirable. It has been shown that electrical detection SSMS yields precisions of better than 6% RSD on these same Kirk standards [7].

Results

Approximately five bullets from each of the ten boxes were analyzed by SSMS

TABLE 2—Analysis of three sections of a single bullet.

Section	B	Al	S	Cl	K	Ca	Ni	Cu	As	Se	Ag	Cd	Sn	Sb[a]	Te	Tl	Bi
									Element, ppm								
Nose	0.04	0.12	19	1.4	1.1	0.2	1.3	104	257	0.7	21	4.0	6.2	0.51	41	3.8	174
Middle	0.02	0.08	21	0.8	0.8	0.3	1.5	143	282	0.4	27	3.2	5.7	0.77	35	3.0	158
Base	0.02	1.1	19	2.4	11.4	2.5	1.7	145	313	0.6	37	4.5	6.6	1.00	44	3.6	280
RSD, %	33	...	5.8	...	...	...	13	17	10	26	29	17	7.4	32	11	12	32

[a] Percent.

TABLE 3—*Precision of analysis of Kirk lead standards using photographic detection.*

	Element, ppm					
Lead Standard	Cu	As	Ag	Sn	Sb[a]	Bi (+2)
Kirk A626						
Certified	780	...	124	...	0.72	1000
SSMS Run 1	460	15	120	130	0.32	74
SSMS Run 2	630	14	117	180	0.32	73
RSF[b]	0.70	...	0.96	...	0.44	0.074
Kirk 604						
Certified	8.0	1000	...	5000	2.12	290
SSMS	5.4	1290	4.9	6300	0.85	23
RSF	0.67	1.29	...	1.26	0.40	0.079

[a] Percent.
[b] Relative sensitivity factor (RSF) defined as SSMS/certified.

and by NAA. The results are shown in Table 4. The average relative deviation of the values obtained by the two methods is 38% for Cu, 27% for As, and 22% for Sb. (The values of Cu and As less than 50 ppm were excluded from this calculation because the NAA values are very uncertain in this range.) Since the NAA method is by far the most accurate, the deviations largely reflect the inaccuracy of SSMS. The main reason for the accuracy being generally poorer than the precision is that standards were not run after each sample. Instead, the usual procedure was to run a Kirk standard before a series of runs requiring several days to complete. In order to convert precision into accuracy, it will probably be necessary to run a standard every day.

The most obvious result in Table 4 is that the bullets in each box do not have uniform elemental compositions. The exception is antimony, which is usually the only element of specified concentration in bullet lead. Closer examination of the table reveals that there are groups of bullets within each box which do have similar compositions. For example, in the Winchester box manufactured 7-22-63, Bullets 1 through 4 are very similar. Bullets 5 and 6 are also similar, but clearly distinct from the others on the basis of As, Se, Cd, and Hg. Other easily spotted groups are S&W Bullets 1, 3, and 5; Speer Bullets 2 and 4; and Browning Bullets 1 through 4.

This grouping of bullets within boxes has not been reported in any of the previous studies. There are probably two reasons for this. The first is that the other methods did not routinely examine enough bullets from each box. If only 2 to 4 bullets per box are examined, as was done by Lukens et al [1] by NAA, it is easy to dismiss the errant Cu and As values as experimental error or "inherent" variation. The second reason is that none of the other studies determined as many elements as reported here.

Grouping Procedure

A consistent method is needed for grouping the bullets according to similar elemental compositions. A general solution for similarity problems has been given by Parker [6]. He has defined the discrepancy index C as

$$C = \sum_{i}^{N} D_i^2 \tag{1}$$

TABLE 4—Results of bullet analysis.

Bullet	S	Cu	As	Se	Ag	Cd	Sn	Sb[a]	Te	Hg	Tl	Bi
Remington												
1	0.6	760 (573 ± 10)[b]	0.8	<0.2	31	1.9	<0.2	0.81 (0.69 ± 0.02)	6.1	<0.3	8.9	540
2	2.5	1000 (549)	1.0	<0.2	39	3.9	<0.2	(0.68) (0.64)	9.5	<0.3	12	840
3	1.1	790 (564)	1.4	<0.2	34	2.5	<0.2	0.61 (0.72)	7.4	<0.3	13	630
4	1.0	950 (612)	0.5	<0.2	27	2.1	<0.2	0.78 (0.71)	4.3	<0.3	8.8	430
5	0.7	750 (486)	0.5	<0.2	26	1.4	<0.2	0.86 (0.60)	3.8	<0.3	12	560
6	1.6	940 (605)	0.6	<0.2	27	1.9	<0.2	0.91 (0.75)	5.0	<0.3	10	470
Browning												
1	120	740 (260 ± 20)	940 (580 ± 70)	<0.2	34	4.9	6400	3.7 (3.08 ± 0.04)	14	38	4.6	190
2	85	420 (250 ± 30)	670 (580 ± 30)	<0.2	33	2.9	6800	3.6 (2.97 ± 0.20)	18	32	3.9	230
3	100	400 (260 ± 10)	660 (560 ± 60)	<0.2	27	5.0	5600	3.4 (3.07 ± 0.07)	25	51	4.7	240
4	73	510 (280 ± 20)	680 (550 ± 30)	<0.2	43	3.6	8400	5.3 (3.14 ± 0.18)	23	43	5.1	260
5	20	670 (450 ± 80)	650 (790 ± 160)	<0.2	23	3.4	1000	4.7 (3.32 ± 0.48)	57	86	5.3	180
Federal												
1	28	260 (291)	610	1.0	24	6.2	6.1	1.2 (1.4)	46	<0.3	4.7	180
2	90	630 (332)	470	0.8	62	17	180	1.4 (1.2)	35	<0.3	7.5	370
3	45	620 (378)	440	0.4	24	8.1	92	1.6 (1.3)	30	<0.3	3.1	160

TABLE 4—Continued.

Bullet	S	Cu	As	Se	Ag	Cd	Sn	Sb[a]	Te	Hg	Tl	Bi
4	130	640 (391 ± 20)	600	1.4	57	23	190	1.4 (1.3 ± 0.07)	110	<0.3	8.9	330
S & W												
1	120	870 (560 ± 30)	530 (490 ± 90)	0.8	25	4.6	5000	5.0 (3.4 ± 0.13)	120	<0.3	3.0	150
2	120	100 (80 ± 10)	1200 (930 ± 150)	<0.2	32	0.3	6200	5.9 (3.3 ± 0.34)	96	<0.3	2.8	160
3	160	1100 (570 ± 40)	600 (500 ± 100)	1.4	33	7.9	6300	4.0 (3.3 ± 0.12)	160	<0.3	5.0	190
4	53	110 (60 ± 20)	1600 (960 ± 190)	0.7	39	0.9	6700	5.3 (3.4 ± 0.32)	100	<0.3	49	170
5	150	990 (590 ± 40)	430 (500 ± 50)	1.6	28	6.2	6000	3.9 (3.6 ± 0.06)	140	<0.3	3.5	190
Speer												
1	76	310 (430 ± 40)	890 (1080 ± 220)	<0.2	24	<0.2	1600	3.2 (3.7 ± 0.39)	18	<0.3	17	100
2	140	260 (150 ± 60)	900 (980 ± 170)	<0.2	40	<0.2	7.9	2.8 (3.5 ± 0.56)	16	<0.3	61	190
3	260	620 (410 ± 10)	1300 (1050 ± 10)	<0.2	51	<0.2	3200	2.8 (3.9 ± 0.31)	36	<0.3	26	180
4	190	380 (170 ± 20)	1400 (920 ± 110)	<0.2	53	<0.2	3.0	3.8 (3.5 ± 0.30)	18	<0.3	47	190
5	70	300 (220 ± 10)	1100 (780 ± 60)	<0.2	48	<0.2	3700	4.0 (3.9 ± 0.08)	29	<0.3	16	160
Winchester (7-22-63)												
1	43	180 (163 ± 20)	510	1.2	41	0.7	<0.2	2.6 (2.2 ± 0.18)	33	1.3	5.3	250
2	48	215 (168)	380	2.0	57	1.5	<0.2	2.0 (2.1)	46	1.9	4.0	230
3	43	200 (153)	470	1.5	52	0.5	<0.2	2.7 (2.2)	57	1.0	3.8	220

Sample												
4	61	220 (152)	480	1.9	60	0.9	<0.2	2.2 (2.1)	65	2.1	5.7	250
5	73	460 (174)	47	0.3	80	17	<0.2	2.4 (2.2)	30	<0.3	5.2	330
6	81	320 (149)	38	0.5	56	19	<0.2	2.2 (2.0)	38	<0.3	3.1	320
Winchester (3-15-72)												
1	74	40 (60 ± 10)	1.1 (30 ± 10)	<0.2	18	2.1	0.2	0.47 (0.51 ± 0.02)	0.4	<0.3	0.9	130
2	34	26 (60)	0.8 (40)	<0.2	11	1.7	0.2	0.46 (0.50)	0.2	<0.3	0.8	80
3	75	55 (60)	6.6 (0)	<0.2	17	6.6	0.2	0.65 (0.48)	0.8	<0.3	0.9	100
4	120	40 (70)	1.5 (20)	<0.2	18	3.4	0.2	0.63 (0.53)	0.5	<0.3	1.6	150
5	85	61 (70 ± 10)	7.8 (10 ± 10)	<0.2	28	12	<0.2	0.78 (0.53 ± 0.01)	1.6	0.7	2.0	140
Winchester (3-22-73, Box 1)												
1	19	66 (70 ± 10)	23 (40 ± 50)	0.3	21	3.7	<0.2	0.52 (0.46 ± 0.03)	4.8	<0.3	2.3	68
2	7.9	40 (40)	19 (30)	<0.2	7.1	6.0	<0.2	0.67 (0.55)	1.6	3.6	2.5	27
3	5.7	16 (20)	3.9 (0)	<0.2	7.0	11	<0.2	0.61 (0.46)	0.5	0.5	2.8	13
4	6.8	40 (40)	21 (20)	<0.2	8.2	5.0	<0.2	0.83 (0.57)	1.2	2.4	2.3	32
5	9.0	14 (20)	11 (10)	<0.2	5.9	11	<0.2	0.66 (0.50)	0.7	<0.3	1.6	17
Winchester (3-22-73, Box 2)												
1	4.1	12 (40 ± 40)	4.4 (20 ± 20)	<0.2	5.0	14	<0.2	0.73 (0.52 ± 0.03)	0.4	<0.3	1.8	8.1
2	4.6	13 (20)	5.4 (10)	<0.2	5.0	13	<0.2	0.68 (0.53)	0.5	<0.3	2.2	9.2
3	25	58 (50)	21 (30)	0.5	28	4.5	<0.2	0.44 (0.44)	8.2	<0.3	1.8	87
4	19	44 (60)	14 (40)	0.4	17	3.0	<0.2	0.55 (0.46)	5.2	<0.3	1.7	67

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TABLE 4—Continued.

Bullet	S	Cu	As	Se	Ag	Cd	Sn	Sb[a]	Te	Hg	Tl	Bi
					Element, ppm							
5	32	120 (180)	16 (10)	0.9	35	1.6	<0.2	0.43 (0.50)	8.1	<0.3	2.2	120
Winchester (4-17-73)												
1	11	58 (60 ± 60)	16 (40 ± 10)	0.5	18	9.4	<0.2	0.60 (0.51 ± 0.05)	3.0	4.2	2.9	47
2	22	53 (60)	21 (30)	0.8	19	13	<0.2	0.70 (0.53)	2.9	3.4	2.3	38
3	14	55 (80)	100 (100)	0.3	16	4.0	<0.2	0.81 (0.54)	12	<0.3	0.8	53
4	12	22 (20)	8.3 (30)	<0.2	10	11	<0.2	0.72 (0.47)	0.7	<0.3	1.9	14
5	3.4	22 (30)	7.7 (10)	0.3	11	9.0	<0.2	0.73 (0.43)	0.9	1.8	2.5	20

a Percent.
b NAA results (±1σ on three runs) are given in parentheses.

where N is the number of attributes and D_i is the reduced deviation of attribute i. For our purposes it will be given by

$$D_i = \frac{X_i - \overline{X}_i}{\sigma_i} \qquad (2)$$

where $\overline{X}_i$ is the mean concentration of element i in the group, σ_i is the standard deviation of element i, and X_i is the concentration of element i for a member of the group. If the D_i's are independent, the values of C are expected to be distributed as chi-square with N degrees of freedom. In that case, the tables of this function can be used to estimate the probability of a given C occurring. We will define this probability as the *similarity* of the bullet to the group. Complete justification of using the chi-square distribution in this way will be postponed until later.

The grouping procedure was as follows:

1. Make an initial grouping using a very liberal criterion such that no bullet could possibly be omitted from its proper group. This likely will mean that some bullets will be placed in groups to which they do not belong.

2. Calculate the discrepancy indices using Eqs 1 and 2 for each bullet and its assigned group. Use the average of all the group standard deviations as an estimate of σ_i in Eq 2. The corresponding similarities may be found in the chi-square tables.

3. Reject all bullets from their groups which yield a similarity of 0.01 or less.

4. Regroup the rejected bullets and repeat Steps 2 and 3 until all grouped bullets have similarities of 0.01 or greater.

Before execution of this procedure, the elemental concentrations were converted to logarithms. This is desirable because the errors in SSMS are expected to be distributed log-normally rather than normally.

The initial criterion in Step 1 was that all elemental concentrations in a group be within a factor of 4. This value was arrived at in the following manner. The highest average error of the SSMS values, taking NAA as correct, was 38% for Cu. This corresponds roughly to a standard deviation of 0.14 in log units. This would be the maximum average standard deviation we would expect for each elemental concentration. The standard deviation of the difference of two concentrations would be $\sqrt{(0.14)^2 + (0.14)^2} = 0.20$. We desire a high level of confidence, so we take 3 times this standard deviation as the criterion ($3\sigma = 0.997$ confidence level). $3 \times 0.20 = 0.60$, which corresponds to a factor of 4. In fact, raising the factor to 5 or even 6 did not change the final groupings.

Grouping Results

Groups were arranged solely according to similarity of elemental concentrations, without regard to box of origin. The results of this procedure are shown in Table 5. Twenty distinct groups were found in the ten boxes, several of these "groups" being single bullets. Of course, it is obvious that had more bullets per box been analyzed, more groups would likely have been found. However, the results strongly suggest that the usual number of groups in a box is only two or three. Undoubtedly, this will depend on the manufacturer and possibly on the caliber as well. Note that the Remington box shows all six bullets in the same group.

Cross-matching occurs between the two Winchester boxes of the same lot (3-22-73)

TABLE 5—Grouping of bullets with similar elemental concentrations—SSMS data.

Group	Remington	Browning	Federal	S & W	Speer	7-22-63	3-15-72	Winchester 3-22-73, Box 1	Winchester 3-22-73, Box 2	Winchester 4-17-73
1	1-6									
2		1-4								
3		5								
4			1							
5			2, 4							
6			3							
7				1, 3, 5						
8				2						
9				4						
10					1, 3, 5					
11					2, 4					
12						1-4				
13						5, 6				
14							1, 2, 4			
15							3, 5			
16								1	3, 4, 5	
17								2, 4	1, 2	1, 2
18								3, 5		4
19										3
20										5

and the box manufactured a few weeks later (4-17-73). However, the Winchester box manufactured 3-15-72, approximately one year earlier, has no bullets similar to the others. Note that all four of these Winchester boxes have the same antimony concentrations and few qualitative differences. They provide a severe test of the differentiation obtained by the method. Except as noted above, all the boxes have unique groups of bullets.

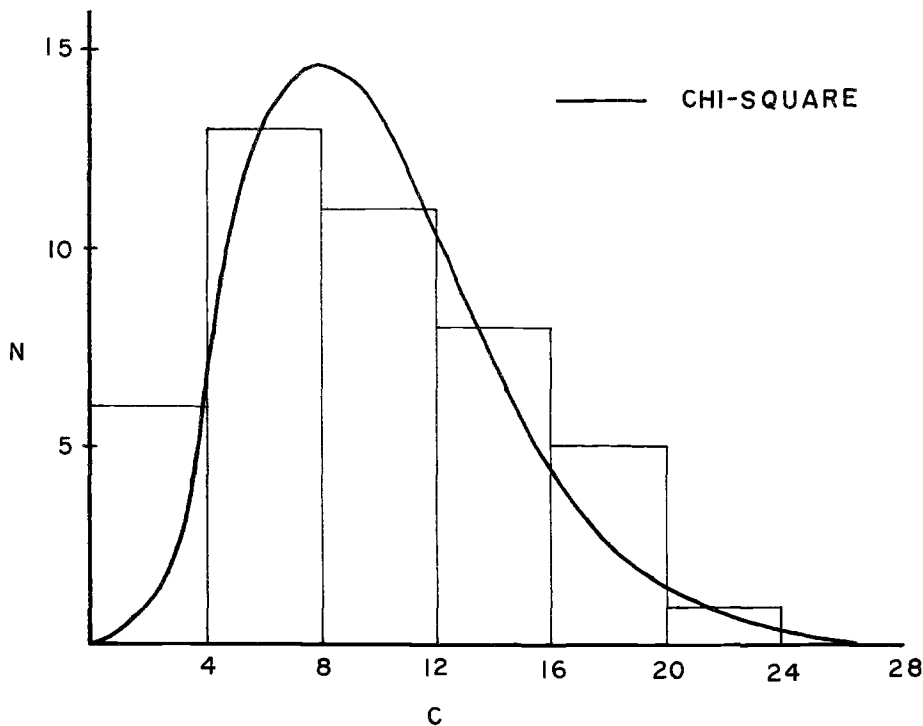Figure 1 is a histogram of the discrepancy indices of the final groupings. Super-

FIG. 1—*Histogram of discrepancy indices from final Groups by SSMS. Smooth curve is chi-square distribution with ten degrees of freedom.*

imposed is the chi-square distribution calculated for ten degrees of freedom. (Ten is the average number of elements determined per sample; twelve is the maximum.) The observed distribution of C was compared with the calculated distribution using the chi-square test. The probability of a match varied from 0.25 to 0.45, depending on the arrangements. Therefore, the assumed chi-square distribution of C is justified.

Rather than giving the entire table of similarities, limits of interest will be noted. The lowest similarity of a group and a member bullet is about 0.01 for Group 14 and Bullet 2 of the Winchester (3-15-72) box. The highest similarity for a group and a nonmember bullet is about 10^{-5} for Group 17 and Bullet 5 of Winchester (4-17-73). It should be considered here that Group 17 does contain some bullets from this box. The highest similarity of a bullet-group pair in which all of the group bullets are from a different box than the test bullet is less than 10^{-10}. On the basis of these calculations, the groups

appear quite distinct. Furthermore, except for the Winchester boxes of 3-22-73 and 4-17-73, there is practically no chance of cross-matching between the boxes.

Grouping by NAA

A simpler procedure may be used for grouping by the NAA data because the standard deviations for many of the bullets were experimentally determined. The averages from Table 4 are as follows:

Element	Concentration Range	θ_i	
Cu	all	27	ppm
As	>200 ppm	100	ppm
As	<200 ppm	20	ppm
Sb	>2.0 %	0.23	%
Sb	<2.0 %	0.04	%

The discrepancy indices for all of the bullet pairs were calculated using Eqs 1 and 2 with $\sigma_i = \sqrt{\theta_i^2 + \theta_j^2}$. Those bullet pairs which had similarities of 0.01 or greater were put in the same groups. The results are shown in Table 6. Note the cross-matching of bullets between the Browning and Speer boxes, between the S & W and Speer boxes, and between all the Winchesters manufactured in 1972 and 1973. If the more stringent grouping procedure used for the SSMS data is applied to the NAA data, an even greater degree of cross-matching occurs. Also, the calculated similarities showed considerably less distinctiveness of the groups than obtained by SSMS.

An Application

As an example of the application of this method of bullet differentiation, the results of an actual case of armed robbery will be presented. A spent bullet at the scene (Q1) was of the same caliber and general description as six unspent bullets (K1 to K6) found in the suspect's gun when he was apprehended one day later. The striations on Q1 were not sufficiently distinct to determine if it had been fired from the gun.

A preliminary analysis of the bullets by NAA showed that Q1 matched some of the K's in Sb and Cu concentrations. A complete analysis by SSMS yielded the results shown in Table 7. The discrepancy index for each bullet pair was calculated from Eqs 1 and 2 using the average standard deviations derived from the groups of Table 5. The computed similarities are given in Table 8. Q1, K2, and K4 show a great similarity. K1 and K3 are also similar to each other, but clearly distinct from the others, as is true for the K5 and K6 pair. Thus, the six K bullets form three distinct groups of two each. Furthermore, Q1 matches one of these groups with a high level of confidence.

Discussion

What can we now say about the origin of Q1? Did it come from the same box or lot as the K's? Indeed, we cannot even say the K's all came from the box or lot. All we can

TABLE 6—Grouping of bullets with similar elemental concentrations—NAA data.

Group	Remington	Browning	Federal	S & W	Speer	Winchester				
						7-22-63	3-15-72	3-22-73, Box 1	3-22-73, Box 2	4-17-73
1	1-6									
2		1-4								
3		5			1, 3					
4			1-4							
5				1, 3, 5						
6				2, 4	2, 4					
7					5					
8						1-6				
9							1-4	1-5	1-5	1, 2, 4, 5
10							5			
11										3

TABLE 7—*Analysis of bullets from armed robbery case, ppm.*

Element	Bullet						
	Q1	K1	K2	K3	K4	K5	K6
S	7.4	2.2	6.7	2.6	13	29	25
Cu	850	1100	1000	760	1270	790	610
As	37	15	49	18	52	39	82
Se	0.5	<0.1	0.4	<0.1	0.5	0.6	0.3
Ag	21	42	26	40	28	21	20
Cd	1.2	1.6	0.7	1.9	1.2	0.8	0.3
Sn	0.7	1.4	0.5	2.5	0.9	<0.3	<0.3
Sb[a]	1.3	0.85	1.6	0.86	1.4	1.1	1.1
Te	5.4	4.3	4.4	4.8	4.8	61	49
Tl	5.2	9.3	6.3	12	9.0	8.2	8.6
Bi	103	420	130	410	105	115	97

[a] Percent.

TABLE 8—*Similarities from armed robbery case.*

Bullet	Bullet						
	Q1	K1	K2	K3	K4	K5	K6
Q1	1.0	<0.01	0.95	<0.01	0.85	<0.01	<0.01
K1		1.0	<0.01	0.98	<0.01	<0.01	<0.01
K2			1.0	<0.01	0.90	<0.01	<0.01
K3				1.0	<0.01	<0.01	<0.01
K4					1.0	<0.01	<0.01
K5						1.0	0.50
K6							1.0

say is that Q1 is indistinguishable from K2 and K4 and therefore "probably" was derived from the same "source" as the two K's. In order to make a definitive statement for identification purposes (that is, to link the suspect with Q1), we need to answer two questions:

1. What is the "source"? Our method of examination defines the source to be a homogeneous batch of lead from which the bullet is produced. Since we have examined only boxes of bullets, we cannot say exactly what constitutes a homogeneous batch of lead. It may be a length of bullet wire, a pig, a heat, or some other physically identifiable entity.

2. What is the probability of occurrence of a given source, or one that is indistinguishable from it? This is equivalent to the probability that the suspect would have a bullet indistinguishable from Q1 merely by chance and is the essence of the identification problem. It can only be determined through a statistical survey of the source population. Note that examination of bullets by box is not the most efficient way to do this, because we already know that a box is not a source.

It is of interest to discuss the effect that nonuniform boxes will have on the identifica-

tion problem. First, it will have no effect at all on the certainty of an identification. For even if all the bullets in a box were indistinguishable, we still could not call the box the source, for there would doubtless be many other boxes manufactured at the same time having identical composition. In fact, the source of the bullets is the same regardless of the packaging procedure. It is fixed by our method of examination. Thus, the probability of occurrence of a bullet with a given composition is the same whether all the bullets in a box are identical or not. It follows that the certainty of identification of Q1 with the suspect is the same if two K's match as if all six K's matched.

The effect of haphazard packaging is to reduce the chance of an identification occurring. For example, if only one bullet had been recovered from the suspect, the chances are two to one that it would not have been a match with Q1, in which case no identification would have been possible. With uniform packaging a match would have been obtained, assuming the bullets to have come from the same box.

Conclusions

The spark source mass spectrometric method is definitely superior to instrumental NAA for establishing the similarity of bullets. For this problem, the relative inaccuracy of SSMS is far outweighed by its multielement capability. Use of electrical detection and isotope dilution [7] should increase the accuracy considerably, making the method even more powerful.

The most important discovery of this work is the presence of distinct groups of bullets within boxes. One immediate conclusion is that a suspect bullet cannot be compared against a box as a whole. Instead, the general approach must be to identify the suspect bullet with a particular group of bullets in that box. In effect, the bullet is traced to a homogeneous "batch" of lead from which it was produced. It is not now possible to state what constitutes this homogeneous source, that is, whether it is a pig or heat or some other physically recognizable unit. We can say only that bullet manufacturers generally use two or more such sources during a production run.

To the extent that the boxes sampled in this study are representative, the prospects for bullet identification by elemental analysis are encouraging. It seems very unlikely that bullets of different manufacturers would yield matching bullets. However, the data on the Winchester boxes indicate that there may be a problem distinguishing bullets of the same caliber manufactured by the same company within a short period of time. The final evaluation of the method for identification purposes must await a more comprehensive study involving different calibers and larger, random samples of the bullet population.

Summary

A study has been made to demonstrate the capability of spark source mass spectrometry (SSMS) for differentiating bullets on the basis of elemental composition. Twenty-six elements are commonly found in bullet lead at the 0.1-ppm level and above. Only twelve of these prove to be generally useful for quantitative characterization.

The precision of analysis with SSMS using photographic detection is about 10% relative standard deviation. The accuracy obtained in this study is considerably worse than this, about 30% average error. In spite of such large errors, SSMS is shown to be far superior to the more precise method of neutron activation analysis. The reason, of course, is the larger number of elements determined by SSMS.

Bullets do not have uniform elemental compositions within a box or lot. Instead,

there are usually two or three distinct groups of bullets within a given box. Three Winchester boxes representing lots manufactured a few weeks apart showed common groups among them. All other boxes had unique groups of bullets, indicating that this method is a promising alternative to the conventional method of identifying bullets by physical markings.

References

[1] Lukens, H. R., Schlesinger, H. L., Guinn, V. P., and Hackleman, R. P., Atomic Energy Commission Report GA-10141, Gulf General Atomic, San Diego, Calif., June 1970.

[2] Brunelle, R. L., Hoffman, C. M., and Snow, K. B., *Journal of the Association of Official Analytical Chemists,* Vol. 53, 1970, p. 470.

[3] Guy, R. D. and Pate, B. D., *Journal of Forensic Sciences,* JFSCA, Vol. 18, No. 2, April 1973, pp. 87-92.

[4] Goode, G. C., Wood, G. A., Brook, N. M., and Coleman, R. F., "Multi-Element Analysis of Glass Fragments by Neutron Activation and the Application to Forensic Science," Atomic Weapons Research Establishment Report No. 024/71, Aldermaston, U.K., 1971.

[5] Schlesinger, H. L., Lukens, H R., Bryan, D. E., Guinn, V. P., and Hackleman, R. P., "Forensic Neutron Activation of Bullet Lead Specifimens," Atomic Energy Commission Report GA-10142, Gulf General Atomic, San Diego, Calif., June 1970.

[6] Parker, J. B., *Journal of the Forensic Science Society,* Vol. 7, 1967, p. 134.

[7] Haney, M. A. and Gallagher, J. F., *Analytical Chemistry,* Vol. 47, 1975, p. 62.

[8] Ahearn, A. J. in *Trace Characterization—Chemical and Physical,* W. W. Meinke and B. F. Scribner, Eds., National Bureau of Standards Monograph 100, Washington, D.C., 1967, pp. 347-376.

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