

Analysis and Comparison of Bullet Leads by Inductively-Coupled Plasma Mass Spectrometry

REFERENCE: Keto RO. Analysis and comparison of bullet leads by inductively-coupled plasma mass spectrometry. *J Forensic Sci* 1999;44(5):1020–1026.

ABSTRACT: Inductively-coupled plasma mass spectrometry (ICPMS) was used to determine eight elements in 9-mm bullet lead from 12 manufacturers. The purpose was two-fold: 1) to develop a feasible ICPMS method for bullet lead analysis, and 2) to observe the range of variability in elemental compositions for bullet lead from diverse sources. The first of these was significantly aided by reduction of the lead concentration by precipitation; the second was demonstrated by the application of numerical correlation analyses to the data.

The results showed that good reproducibility ($\pm 5\%$ relative standard deviation) and sensitivity (generally in the sub-part-per-million range) can be obtained. No bullets from different sources had similar elemental signatures, whereas very different signatures could be found within a single box of bullets. Numerical criteria were developed to separate “matching” bullets from all different-source bullets for the subject population.

KEYWORDS: forensic science, elemental analysis, bullet, lead, inductively-coupled plasma mass spectrometry, ICPMS

The identification of bullet lead can provide useful information in the solving of crimes involving the use of firearms. In some shooting situations, bullets from the crime scene may be too deformed for ballistic-type comparisons, or the firearm may not be recovered for the production of known ballistic samples. In such cases, unfired bullets recovered from a suspect or his property can be compared against the crime scene bullets through elemental analysis. The result of this type of comparison would be that the suspect bullets are consistent with (or could have come from) the same source as the known bullets.

Instrumental methods that have been used for the trace elemental analysis of bullet lead include atomic absorption spectrometry (AAS) (1–5), neutron activation analysis (NAA) (4–11), spark source mass spectrometry (SSMS) (12,13), inductively-coupled plasma emission spectroscopy (ICP-AES) (14–16), and inductively-coupled plasma mass spectrometry (ICP-MS) (17,18). Each of these methods has its advantages and limitations. AAS and NAA are limited in the number of elements that can be conveniently analyzed, with most studies concentrating on only three or four elements. SSMS, ICP-AES, and ICP-MS are applicable to a wide range of elements, with the mass spectrometric techniques sharing a distinct sensitivity advantage over the emission spectroscopic

technique. Of the two mass spectrometric techniques, the spark-source method requires less sample preparation and has fewer interferences, whereas the ICP method has better analytical precision.

ICP-MS was used in this study to analyze trace elements in bullet lead from a variety of sources. ICP-MS is well suited to the analysis of bullet lead because of its low detection limits and many orders of magnitude of linear response. As a result, comparative information can be gained from bullet fragments as small as 10 mg using conventional dilution and aspiration techniques. The main drawback to using ICP-MS is that the sample matrix (lead) causes significant signal suppression for trace elements (19), and builds up rapidly (as the oxide) on the sampling cone, thereby reducing ion throughput and producing erratic results. These drawbacks are largely circumvented by precipitating the lead with sulfuric acid.

The sample preparation method was adapted from Peters et al. (14) with modifications to accommodate the lower sample weights and concentrations utilized in ICP-MS. Additionally, the method of Suzuki and Marumo (17) was incorporated to reduce the lead matrix concentration to a level commensurate with the ICP-MS technique.

Euclidean distances and correlation values (20,21) were calculated for the comparison of each bullet against each of the other bullets analyzed. Numerical criteria were developed as a measure of the likelihood that two bullets have the same or indistinguishable elemental profiles.

Materials and Methods

Instrument

The instrument used for this work was a Fisons/VG Elemental Eclipse ICP-MS that had been upgraded by the manufacturer to the equivalent of their Genesis model, primarily by substitution of an electron multiplier for the Faraday cup detector. Standard equipment included a double-pass borosilicate glass spray chamber, Meinhard type A nebulizer, and nickel sampling and skimmer cones. The plasma was controlled by a 27 MHz self-oscillating generator running on the low power setting. Both the spray chamber and sampling interface were cooled to 10°C by circulating water, and the torch (coolant/auxiliary) argon flow was 16 lpm. The instrument was tuned daily to give a relatively flat response in the 65 to 209 amu region, with an absolute response of approximately 400,000 cps for 20 ng/mL ¹¹⁵In solution. The elemental isotopes analyzed were ⁶³Cu, ⁷⁵As, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁸Sn, ¹²¹Sb, ¹²⁶Te, and ²⁰⁹Bi, with a dwell of 1000 ms at each of 3 points per peak.

Materials and Reagents

Nitric, sulfuric, and hydrofluoric acids were Fisher Tracemetal Grade (Fisher Scientific, Pittsburgh, PA). Bullet lead reference

¹ Forensic chemist, National Laboratory Center, Bureau of Alcohol, Tobacco, and Firearms, Rockville, MD.

Received 1 Sept. 1998; and in revised form 24 Nov. 1998; accepted 27 Nov. 1998.

TABLE 1—*Bullet samples.*

U.S. Producers
CCI Blazer, A. Blount, Inc., Lewiston, ID
Federal Cartridge Co., Anoka, MN
Olin Winchester Group, East Alton, IL
Super-Vel, H&H Cartridge Co., Greensburg, IN
Union Metallic Cartridge Co., Remington Arms, Inc., Lonoke, AR
Foreign/Imported
Anguila, Cartuchos Deportivos De Mexico, S.A., Cuernavaca, Morelos, Mexico
Defence Industries, Canada
Fabrica Nacional de Toledo, Spain
Interarms, Alexandria, VA, (Produced in Czech Republic)
Musgrave, Pretoria Metal Pressings, Ltd., South Africa
PMC, Eldorado Cartridge Corp., Boulder City, CO (Produced in Korea)
Rio, Southern Gun Distributors, Opa-Laka, FL (Produced in Brazil)

standards consisted of NIST Standard Reference Materials (SRM's) C-2416 Bullet Lead and C-2418 High Purity Lead (National Institute of Standards and Technology, Gaithersburg, MD), and BCR Certified Reference Materials (CRM's) 286 Electrolytically Refined Lead and 288 Lead with Added Impurities (Community Bureau of Reference, Commission of the European Communities, Brussels, Belgium). Indium (NIST SRM 3124a) was used as an internal standard in all standard and unknown solutions. The interference of ^{115}Sn on ^{115}In was found to be significant (0.34%) for samples with high tin content. Accordingly, the results for these samples and standards were corrected for this interference. It is recommended that another internal standard (such as yttrium) be used in future work.

Unknown bullet samples consisted of 12 boxes of 9 mm Luger ammunition that were on hand (see Table 1). Deionized water was produced in-house. All dilutions were done with standard Pyrex volumetric glassware that had been properly cleaned and soaked in 20% HNO_3 for at least 24 h prior to use.

Sample Preparation

Five bullets were drawn from each box in a diagonal pattern from upper left to lower right corner. Each was sampled by filing the nose flat (thereby removing copper jacket material) and drilling with a $\frac{1}{8}$ -in. (3 mm) drill at very slow (110 rpm) speed to avoid melting. Initial cuttings were discarded to remove surface copper that may have transferred from the jacket during filing. 25 mg of the deeper cuttings were accurately weighed on a microbalance (Cahn Model C-33) in triplicate and placed in 15 mL polypropylene centrifuge tubes. 2.0 mL 25% HNO_3 ² containing .5% HF were added to each tube, which was then capped tightly and heated at 80°C until the metal had completely dissolved (typically 1 to 3 h). After cooling the tubes, 8.0 mL 5% H_2SO_4 were added, immediately followed by capping and gentle inverting and reverting approximately once per second for ten inversions. After settling for several minutes, the precipitate was re-dispersed by mixing for 5 seconds on a vortex mixer (Fisher Genie 2) set on high speed. The precipitate was then allowed to settle for 1 h, and was further re-

moved by centrifuging at 3000 rpm for 10 min. 5 mL of the supernatant was placed in a 25 mL volumetric flask, along with 1.0 mL 1250 $\mu\text{g}/\text{L}$ internal standard and 1.0 mL 0.50% HF, and diluted to the mark with 1% HNO_3 .

Recovery study samples were produced by placing 25 mg samples of known lead standards in centrifuge tubes and digesting them as above. Blank samples were produced by placing 2.0 mL 25% HNO_3 /.5% HF in empty centrifuge tubes and following the addition and dilution steps.

Lead Standards

Four different lead standards were used in this work. NIST SRM C2416 was used in the quantitation of Cu, As, Ag, Sn, Sb, and Bi. NIST SRM C2418 was used as a background subtract standard and as a diluent for SRM C2416 to produce an intermediate concentration standard. BCR CRM 288 was used in the quantitation of Cd and Te, and to provide additional points on the calibration curves for the other elements at lower concentrations. BCR CRM 286 was used as a background subtract standard and as a diluent with CRM 288 to produce an intermediate concentration standard for Cd and Te. Thus, six standards (consisting of a two background subtract standards, two intermediate standards, and two high standards) were run.

Standard stock solutions were made by accurately weighing 2.5 g of each lead standard into a 200 mL volumetric flask, adding 100 mL 50% HNO_3 , and heating on a moderate hot plate until dissolved. After cooling, 1.0 mL HF was added, and the contents were diluted to the mark with deionized water.

Standard working solutions were made by pipetting 2.0 mL of the stock solution into a centrifuge tube and following the same procedure used for the bullets (heating, cooling, precipitation, clarification, additions, and dilution).

Experimental Design

Final dilutions of all blanks, standards, and samples were placed in fresh 15 mL polypropylene centrifuge tubes for analysis. Six replicate elemental scans for the eight elements of interest were performed on each tube. Four sets of standards were run, one at the beginning, one at the end, one between the first and second sample sets, and one between the second and third sample sets. Each of the sample sets contained one weighing for each of the five bullets sampled per box. This resulted in the three replicate weighings for each bullet being separated by standard runs. The sample order within each set was also varied to average out any systematic drift in instrumental response.

After the analytical run, the procedure file was edited into three separate files (one for each sample set) with each set being preceded and succeeded by standards in the consecutive order in which they were run. Calibration curves were calculated by incorporating responses from both sets of standards. This allowed a visual appraisal of instrumental drift during the run, and assured that the sample results were as accurate as practicable. A typical calibration curve, which also shows the linearity between the European and U.S. standards, is shown in Fig. 1.

Results and Discussion

Recovery Study

The results for the recovery study are shown in Table 2. These data are averages for three sets of triplicate 25 mg weighings of the respective standards, that were digested and processed as samples.

² Solution strengths refer to mL of the full-strength acid in 100 mL acid solution; full-strength for the acids were as follows: HNO_3 = 68–71%; H_2SO_4 = 95–98%; HF = 48–51%.

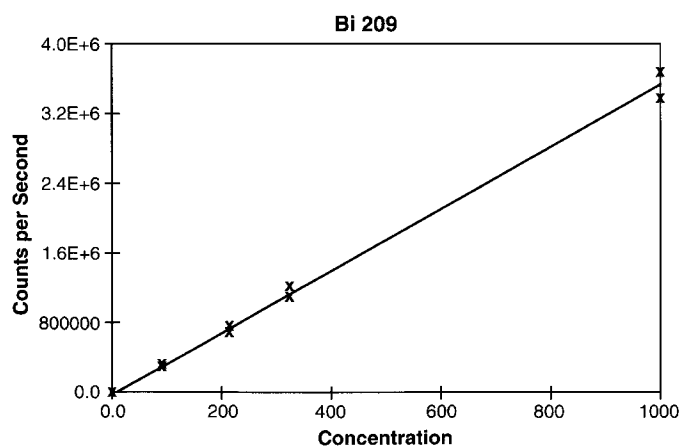


FIG. 1—Typical calibration curve (bismuth); points at 97 and 216 $\mu\text{g/g}$ are for diluted and undiluted BCR standard, respectively; points at 326 and 1000 $\mu\text{g/g}$ are for diluted and undiluted NIST standard, respectively. Dual points at each concentration are for measurement of each standard before and after the analytical run.

TABLE 2—Analytical results for reference materials ($\mu\text{g/g}$).

	BCR CRM 288		NIST SRM C2416	
	Found	Certified	Found	Certified
Cu	19.5 ± 0.8	19.3 ± 0.4	677 ± 21	650 ± 20
As	53.7 ± 1.2	55.7 ± 1.6	554 ± 13	560 ± 10
Ag	29.4 ± 0.5	30.5 ± 0.5	43 ± 2.6	44 ± 2
Cd	32.4 ± 0.5	33.3 ± 0.9	—	—
Sn	31.3 ± 2.2	30.6 ± 1.5	895 ± 21	900 ± 100
Sb	31.5 ± 0.6	32.5 ± 0.9	7714 ± 200	7900 ± 100
Te	31.9 ± 0.5	32.8 ± 1.3	—	—
Bi	219 ± 5.0	216 ± 2.4	978 ± 34	1000 ± 100

TABLE 3—Instrumental response for NIST C-2416 reference material (Integrated Counts).

Element	Non-Precipitated	Pb Precipitated
Cu	2,130,000	3,480,000
As	269,000	402,000
Ag	846,000	1,324,500
Sn	314,000	462,000
Sb	283,000	385,000
Bi	395,000	704,000

The data show that the precipitation step does not affect analytical results for the elements of interest. Table 3 shows the relative signal strengths for precipitated and non-precipitated samples of the NIST C2416 lead. The increase in signal for the precipitated sample is presumably due to the reduction of matrix effects (signal suppression) by the lead (19).

Bullet Results

The bullet compositions are listed in Table 4. These data are based on the three replicate weighings for each sample, and therefore contain variability due to weighing, dilution, and

instrumental reproducibility. Values of zero indicate that one or more of the replicates was zero for that element. The data show a wide range of compositions from brand to brand as well as within brands. Since only five bullets were sampled from each box, these numbers do not represent all possible compositions among the bullet population; however, the data do give an indication of the range and variability expected for 9 mm jacketed bullets. The occurrence of multiple compositions within boxes of ammunition has been reported (13,16), and is largely due to mixing of lead slugs from different melts or “pigs” in the manufacture of finished cartridges.

When comparing element profiles, small differences between individual elements become less significant as the number of elements analyzed increases. Lukens et al. (6) determined three elements (antimony, copper and arsenic) with good precision and found a “marked negative aspect to the probability of distinguishing between two bullets” by NAA, and recommended analyzing at least six elements. Brunelle et al. (1) determined four elements (antimony, copper, bismuth, and silver) with moderate precision by atomic absorption, and found the results promising, but concluded that it “would be highly desirable to detect and measure additional elements” on which to base a comparison. Peele et al. (16) determined six elements with good precision, and found as many as 15 distinguishable element profiles within a single box. Haney and Gallagher (12,13) determined up to 12 elements with rather poor precision, but easily established the presence of multiple groupings within a box, and calculated discrepancy indices for placing profiles into groups (13).

In this study, eight elements were analyzed because they were the ones that were easily determined using the instrumentation, sample preparation procedure, and standards available. The goal was to develop as simple a technique as possible. Four of the 12 elements that have certified values in the standards (zinc, nickel, thallium, and sulfur) were excluded because early tests showed unacceptably high variability attributable to low signal to background ratio. ^{64}Zn and ^{66}Zn , the two most abundant zinc isotopes, are interfered by $^{32}\text{S}^{16}\text{O}_2^+$ and $^{34}\text{S}^{16}\text{O}_2^+$, respectively, from the sulfuric acid used in the lead precipitation step. ^{68}Zn , the third strongest isotope, has an instrumental background due to $^{40}\text{Ar}^{12}\text{C}^{16}\text{O}$. Nickel also has an instrumental background from the nickel sampling and skimmer cones. These backgrounds, combined with the low presence of nickel and zinc in the BCR 288 standard (2.3 and 4.1 ng/mL, respectively, in the final dilution) decreased the precision with which these two elements could be determined. Thallium, the only other element certified in the BCR standard, has a diluted strength of 1.2 ng/mL, and its two isotopes (^{203}Tl and ^{205}Tl) are flanked by isotopes of lead (^{204}Pb and ^{206}Pb), which has a residual concentration approximately four orders of magnitude higher (17). The development of techniques for the precise skimming of the thallium data from the lead background was beyond the scope of this work. The only certified element in the NIST C2416 standard that was excluded was sulfur, for obvious reasons.

The values for antimony in Table 4 show nominal percentages of zero (Federal, Interarms, and Super-Vel), 0.1% (Federal and Olin), 0.4% (Anguila and PMC), 0.7% (PMC, Remington, and Toledo), 1% to 1.25% (Rio and Toledo), 1.25% to 1.5% (Cascade and Defence), and 1.5% to 2% (Cascade and Toledo). It is evident that antimony values can vary significantly among bullets within a box, and that antimony levels overlap from one manufacturer to another. Antimony is not needed to improve hardness in any of these bullets since they all have copper jackets.

TABLE 4—Elemental Compositions of Bullets ($\mu\text{g/g}$).

Brand		Cu	As	Ag	Cd	Sn	Sb	Te	Bi
Anguila	1	135 \pm 7	650 \pm 20	7.0 \pm .08	0	0	3780 \pm 30	.06 \pm .04	95 \pm 1
	2	57 \pm 2	71 \pm 9	6.0 \pm .10	.09 \pm .03	0	3700 \pm 170	.21 \pm .01	86 \pm 3
	3	136 \pm 4	680 \pm 20	6.3 \pm .08	.13 \pm .06	0	3800 \pm 20	.09 \pm .01	96 \pm .3
	4	64 \pm 2	105 \pm 2	6.1 \pm .10	.10 \pm .09	0	3900 \pm 20	.28 \pm .02	87 \pm 2
	5	267 \pm 14	291 \pm 7	6.7 \pm .20	.13 \pm .05	0	3360 \pm 30	.17 \pm .02	98 \pm 4
Cascade	1	79 \pm 5	144 \pm 5	22 \pm 0.1	2.1 \pm .05	970 \pm 20	14300 \pm 900	.13 \pm .03	211 \pm 9
	2	242 \pm 7	134 \pm 2	25 \pm 0.3	2.1 \pm .1	1430 \pm 80	17000 \pm 1300	.10 \pm .02	228 \pm 10
	3	225 \pm 15	115 \pm 10	22 \pm 1.5	2.0 \pm .2	1220 \pm 100	13000 \pm 2600	.06 \pm .03	210 \pm 9
	4	240 \pm 6	126 \pm 4	23 \pm 0.3	2.0 \pm .1	1370 \pm 10	16900 \pm 800	.09 \pm .02	220 \pm 10
	5	247 \pm 5	134 \pm 4	25 \pm 2.0	2.3 \pm .1	1270 \pm 110	18900 \pm 1800	.11 \pm .02	225 \pm 12
Defence	1	7.0 \pm 2	2.9 \pm .2	5.6 \pm .06	.07 \pm .02	0	13400 \pm 300	.10 \pm .02	2.7 \pm .1
	2	246 \pm 2	58 \pm 1	9.4 \pm .2	.45 \pm .04	780 \pm 60	13700 \pm 1300	13.5 \pm .6	13.7 \pm .5
	3	192 \pm 6	16 \pm .4	7.9 \pm .1	.18 \pm .01	40 \pm .7	12800 \pm 1200	1.6 \pm .06	13.4 \pm .9
	4	191 \pm 1	19 \pm .7	6.7 \pm .1	.54 \pm .08	0	12800 \pm 1400	.40 \pm .002	11.0 \pm .6
	5	204 \pm 2	46 \pm 1	8.7 \pm .2	.36 \pm .01	640 \pm 20	14600 \pm 900	11.4 \pm .4	12.6 \pm .4
Federal	1	230 \pm 4	.23 \pm .24	21 \pm .4	.16 \pm .09	.11 \pm .07	26 \pm 4	10.2 \pm .02	108 \pm 3
	2	218 \pm 1	31.5 \pm .3	21 \pm .2	0	.03 \pm .004	908 \pm 6	10.5 \pm .1	108 \pm 4
	3	235 \pm 5	.21 \pm .16	20 \pm .2	.19 \pm .04	.05 \pm .05	28 \pm 1	10.2 \pm .04	108 \pm 4
	4	235 \pm 2	.12 \pm .09	21 \pm .4	0	.01 \pm .01	22 \pm .2	10.3 \pm .1	107 \pm 2
	5	290 \pm 5	.24 \pm .08	20 \pm .2	.45 \pm .03	.08 \pm .03	79 \pm 1	9.3 \pm .2	110 \pm 1
Interarms	1	32 \pm 2	0	51 \pm .7	3.0 \pm .02	0	0	0	214 \pm 4
	2	0	0	52 \pm .3	3.6 \pm .02	0	0	0	222 \pm 2
	3	685 \pm 22	0	12 \pm .3	.66 \pm .05	0	57 \pm 1	.09 \pm .02	421 \pm 12
	4	0	0	23 \pm .3	14 \pm .3	0	0	.14 \pm .01	1250 \pm 21
	5	203 \pm 2	0	25 \pm .4	5.9 \pm .1	0	24 \pm 2	.37 \pm .03	398 \pm 9
Musgrave	1	49 \pm .4	36 \pm 2	76 \pm .3	.24 \pm .01	0	15100 \pm 3500	13 \pm 1	292 \pm 5
	2	42 \pm .5	33 \pm 2	66 \pm 1	.24 \pm .03	0	16000 \pm 2800	12 \pm 1	280 \pm 9
	3	47 \pm .5	36 \pm 2	76 \pm 1	.23 \pm .04	0	14300 \pm 2400	12 \pm .9	279 \pm 2
	4	38 \pm 1	60 \pm 4	58 \pm .6	.58 \pm .01	0	18000 \pm 4100	20 \pm 2	233 \pm 4
	5	48 \pm .6	38 \pm 2	71 \pm 1	.29 \pm .02	0	13800 \pm 1600	13 \pm .5	274 \pm 2
Olin	1	29 \pm 1	.46 \pm .04	8.9 \pm .1	.05 \pm .02	0	1520 \pm 20	2.8 \pm .05	48 \pm 1
	2	42 \pm 16	.39 \pm .02	8.6 \pm .1	.04 \pm .03	0	1060 \pm 10	2.7 \pm .07	48 \pm 1
	3	24 \pm 1	.41 \pm .05	8.8 \pm .1	.03 \pm .02	0	1110 \pm 8	2.8 \pm .01	48 \pm .4
	4	20 \pm 4	.16 \pm .01	8.2 \pm .1	.08 \pm .01	0	453 \pm 6	1.5 \pm .04	42 \pm 1
	5	26 \pm 1	.51 \pm .06	8.9 \pm .1	.05 \pm .02	0	1180 \pm 15	2.7 \pm .05	48 \pm .8
PMC	1	297 \pm 9	1.2 \pm .07	30 \pm .7	.85 \pm .05	0	4140 \pm 110	.49 \pm .03	25 \pm .7
	2	243 \pm 6	10.7 \pm .1	21 \pm .3	.94 \pm .02	306 \pm 8	7240 \pm 170	1.1 \pm .01	52 \pm .8
	3	242 \pm 2	13.0 \pm .4	22 \pm .2	4.4 \pm .1	207 \pm 13	6950 \pm 70	1.7 \pm .01	42 \pm .6
	4	228 \pm 2	12.1 \pm .2	16 \pm .4	1.2 \pm .01	149 \pm 2	7310 \pm 150	1.3 \pm .03	53 \pm .8
	5	233 \pm 5	11.8 \pm .1	19 \pm .4	1.4 \pm .02	177 \pm 6	7300 \pm 70	1.8 \pm .01	46 \pm .4
Remington	1	770 \pm 60	11 \pm .9	20 \pm 1	1.1 \pm .05	0	7400 \pm 180	66 \pm 2	87 \pm 4
	2	771 \pm 40	11 \pm 2	20 \pm 3	1.0 \pm .04	0	7280 \pm 740	61 \pm 3	90 \pm 1
	3	1280 \pm 120	15 \pm .9	22 \pm .5	.31 \pm .01	0	6010 \pm 190	25 \pm 1	100 \pm 5
	4	19 \pm .9	.4 \pm .02	24 \pm 2	.24 \pm .02	0	7400 \pm 150	12 \pm 1	118 \pm 4
	5	762 \pm 50	11 \pm 1	21 \pm 1	1.1 \pm .04	0	7170 \pm 160	68 \pm 2	89 \pm 3
Rio	1	311 \pm 6	988 \pm 20	12.2 \pm .4	3.6 \pm .06	754 \pm 95	12200 \pm 470	4.6 \pm .2	73 \pm .3
	2	285 \pm 5	933 \pm 11	10.1 \pm .6	3.0 \pm .05	639 \pm 71	10000 \pm 320	3.1 \pm .1	55 \pm .2
	3	314 \pm 1	1010 \pm 25	12.7 \pm .3	3.6 \pm .15	790 \pm 16	12500 \pm 330	4.8 \pm .1	74 \pm 1
	4	306 \pm 1	1030 \pm 12	12.7 \pm .3	3.6 \pm .04	781 \pm 18	12500 \pm 290	4.8 \pm .1	74 \pm .7
	5	198 \pm 8	668 \pm 15	11.2 \pm .2	1.6 \pm .08	439 \pm 44	12300 \pm 740	2.5 \pm .06	48 \pm 1
Super-Vel	1	7 \pm 1	0	38 \pm 2	1.2 \pm .02	0	0	.03 \pm .01	283 \pm 27
	2	22 \pm 2	0	18 \pm 1	.77 \pm .05	0	8.7 \pm .2	5.6 \pm .3	373 \pm 18
	3	8 \pm 1	0	18 \pm 1	.77 \pm .05	0	1.3 \pm .1	5.6 \pm .3	294 \pm 34
	4	10 \pm 2	0	38 \pm 2	1.1 \pm .14	0	0	0	267 \pm 11
	5	10 \pm 2	0	40 \pm .5	1.2 \pm .05	0	0	0	267 \pm 4
Toledo	1	58 \pm .3	29 \pm .6	3.4 \pm .2	0	0	11100 \pm 150	.18 \pm .10	1.7 \pm .1
	2	11 \pm 1	10.8 \pm .7	20 \pm .4	.8 \pm .05	0	11000 \pm 640	.22 \pm .02	18 \pm .2
	3	15 \pm 2	8.4 \pm .6	19 \pm .7	.6 \pm .08	0	7000 \pm 460	.21 \pm .01	16 \pm .6
	4	40 \pm 5	20 \pm 2	5.7 \pm .1	0	0	20300 \pm 610	.28 \pm .08	8.0 \pm .3
	5	10 \pm 1	4.2 \pm .4	23 \pm 3	.7 \pm .04	0	8300 \pm 130	.40 \pm .01	20 \pm 2

Data Analysis

Pearson product correlation analyses were performed to see if any of the elements in Table 3 varied in step with any of the other elements. The only significantly high coefficient (.724) was for cadmium versus bismuth. This was determined to be due to a sin-

gle sample (Interarms #4) in which both cadmium and bismuth far exceed any other sample, thereby skewing the analysis. Scatter plots of each element against each of the other elements showed no visual correlations, either linear or non-linear.

Table 5 lists the elemental ranges, means, and medians for the 60 bullets analyzed, averages for standard deviations and coefficients

TABLE 5—Elemental variability ($\mu\text{g/g}$).

	Cu	As	Ag	Cd	Sn	Sb	Te	Bi
Range of Concentrations:	0 to 1278	0 to 1030	3.4 to 72.7	0 to 14.2	0 to 1430	0 to 18900	0 to 67.8	1.7 to 1248
Mean	191	127	22.3	1.29	199	7250	7.2	147
Median	164	11.9	20.0	0.63	0.0	7200	1.6	92
Analytical Precision								
Avg. S.D.*	± 8	± 3	$\pm .5$	$\pm .05$	± 11	± 320	$\pm .2$	± 5
Avg. C.O.V.*	4.3%	2.4%	3.0%	4.0%	5.5%	5.4%	3.3%	4.1%
Detection Limit	1.1	0.02	0.04	0.07	0.6	0.3	0.03	0.2

*(Average standard deviations and coefficients of variation for three replicate weighings).

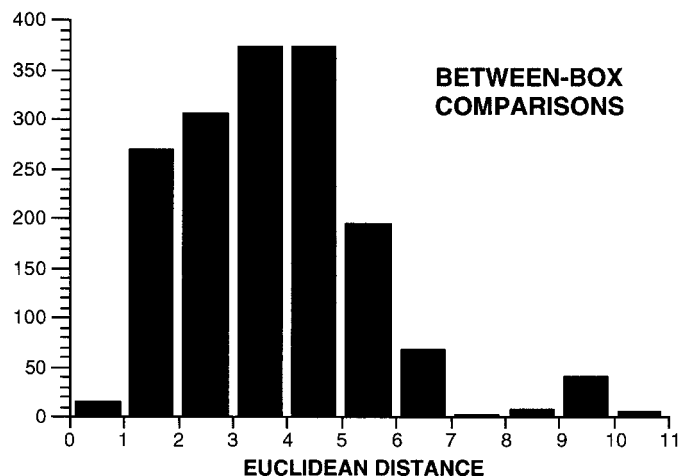
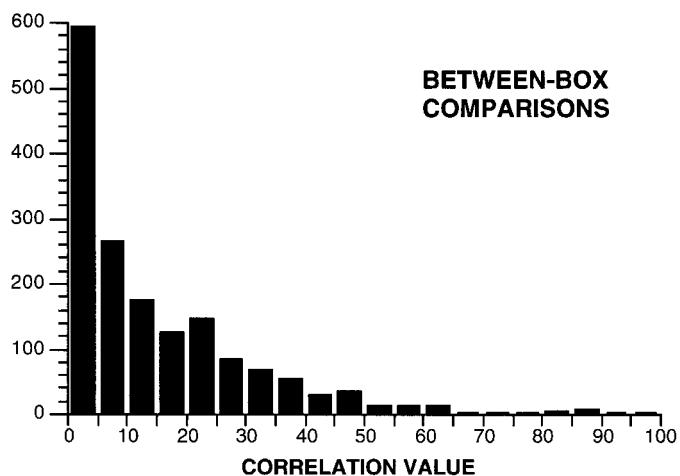
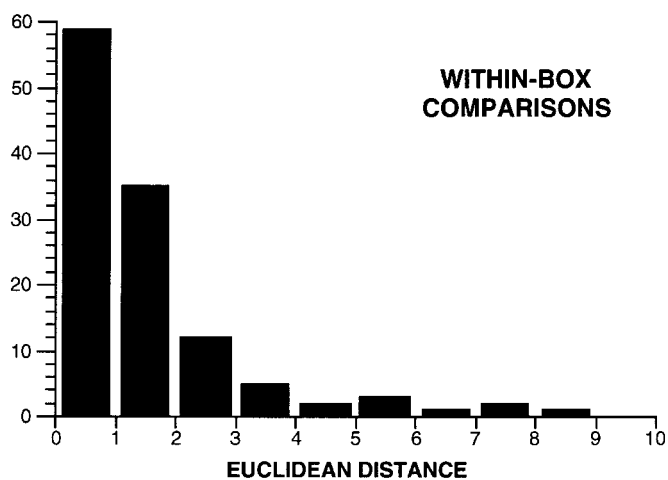
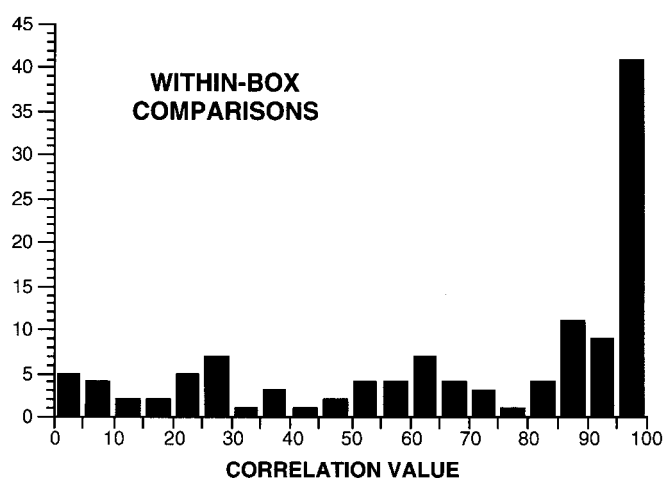


FIG. 2—Distributions for correlation values for within-box comparisons (top) and between-manufacturer comparisons (bottom).

FIG. 3—Distributions for Euclidean distances for within-box comparisons (top) and between-manufacturer comparisons (bottom).

of variation for each determination, and estimated detection limits for the elements. Detection limits were calculated as three times the standard deviations obtained for a system blank run under the same conditions.

Euclidean Analyses

Euclidean distances and correlation values (20,21) were calculated to quantify the extent to which each bullet "matched" each of the other 59 bullets tested, for a total of 1770 individual inter-bul-

let comparisons. By this method, each elemental composition is theoretically plotted as a vector in n -dimensional space, with n equal to the number of elements profiled. Correlation values are determined by the angle between the vectors, whereas Euclidean distance is the linear separation of the ends of the vectors; the evaluation of both parameters gives a higher degree of discrimination than either by itself. A perfect match has a Euclidean distance of zero and correlation of 100.

Feature scaling (22) was applied to the data in Table 4 prior to Euclidean analyses. This was used to overcome the tendency for

high-concentration elements to dominate the comparison, and to give each element equal weight. The average for each column in Table 4 was subtracted from each individual value within the column, and the result was divided by the standard deviation for the column. The resulting numbers center around zero and range from several units negative to several units positive. Euclidean results are not affected by the sign of the data, and are always positive.

Figure 2 shows histograms for correlation values for within-box and between-box (between-manufacturer) comparisons. Clustering at opposite ends for these two populations is expected, inasmuch as bullets from the same box are expected to have similar compositions, and bullets from different manufacturers are expected to be different. However, also evident is the fact that there are bullets within a box that have very different elemental compositions, giving rise to correlations ranging from 95 down to less than 5. Correlation values for the between-box comparisons peak between zero and 5, and increase in rapidly diminishing numbers, with only two of the 1650 intermanufacturer comparisons (0.1%) exceeding 90. The median correlation for same-box comparisons is 85.9, whereas that for between-box comparisons is only 9.2.

Figure 3 shows histograms for Euclidean distances for within-box and between-box comparisons. Here, the differences between the two populations are not as distinct. While the same-box comparisons cluster near zero as expected, the between-

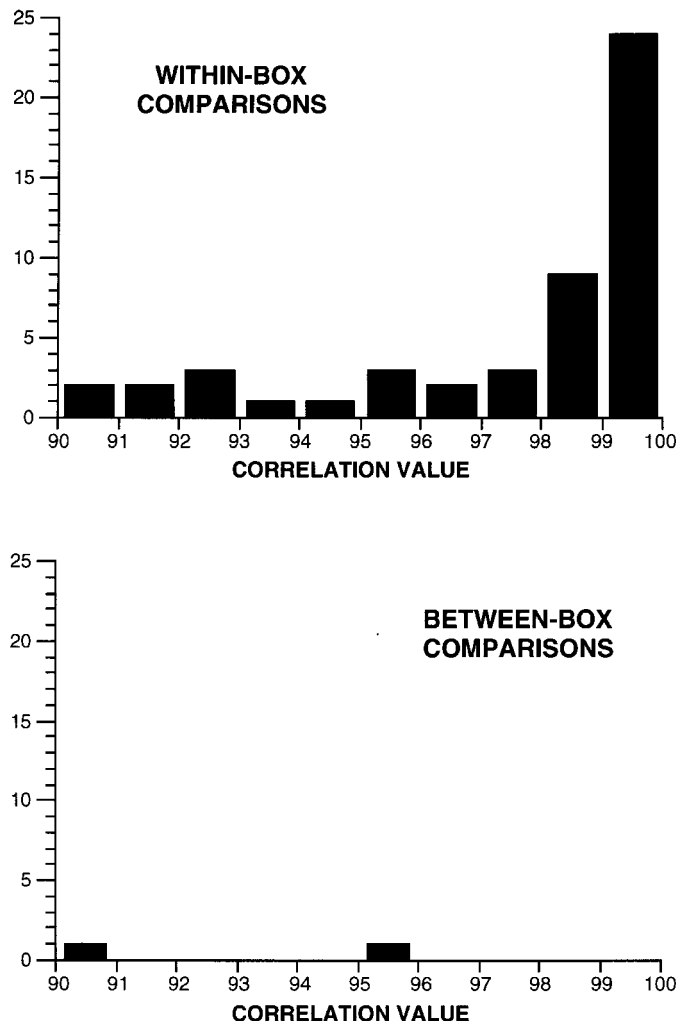


FIG. 4—Expanded-scale distributions for correlation values for within-box comparisons (top) and between-manufacturer comparisons (bottom).

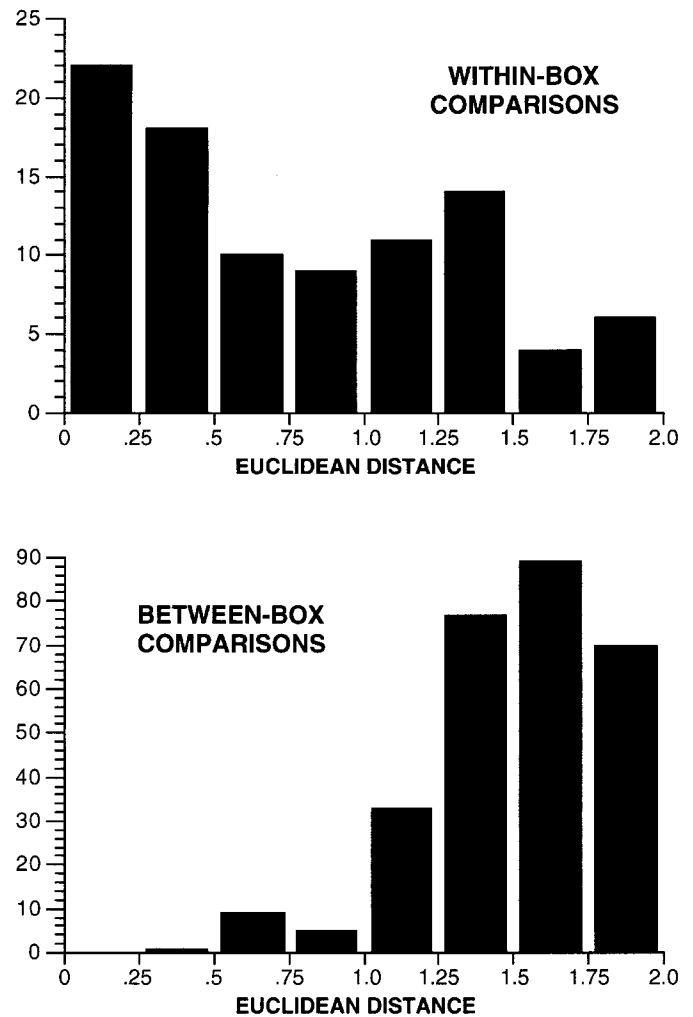


FIG. 5—Expanded-scale distributions for Euclidean distances for within-box comparisons (top) and between-manufacturer comparisons (bottom).

box comparisons show a relatively broad cluster in the center of the range. The median Euclidean distance for within-box comparisons was 1.02 and that for between-box comparisons was 3.68.

Figures 4 and 5 show expanded-scale correlation value and Euclidean distance histograms, respectively, for within-box and between-box comparisons. There is no overlap between the two populations for correlation values greater than 96, or for Euclidean distances less than 0.25. Using these numbers as cut-off values, the total number of within-box comparisons that would be correctly identified as coming from the same source (to the exclusion of all different-source bullets) is 21 (18% of the total of 120 within-box comparisons). These are listed in Table 6. The closest different-source comparison was that of Defence 1 versus Toledo 1, which had a correlation of 95.1 and distance of 0.47. The elemental data for these two samples (Table 4) shows large differences in the copper and arsenic concentrations that would exclude the possibility of these being considered as a match.

Derived data such as correlation values and Euclidean distances are useful in describing global differences in bullets, and in comparing new bullets against all that have been analyzed before. It should be kept in mind, however, that it is not a substitute for direct comparison of the raw elemental data when formulating an opinion

TABLE 6—Euclidean Distances and Correlations for Matching Bullets ($D < 0.25$ and $C > 96$).

Comparison	Distance	Correlation
Anguila 1 vs. Anguila 3	.124	99.85
Anguila 2 vs. Anguila 4	.128	99.37
Cascade 2 vs. Cascade 4	.202	99.85
Defence 3 vs. Defence 4	.229	98.22
Federal 1 vs. Federal 3	.066	99.81
Federal 1 vs. Federal 4	.073	99.81
Federal 3 vs. Federal 4	.108	99.53
Musgrave 1 vs. Musgrave 3	.164	99.82
Olin 1 vs. Olin 3	.064	99.93
Olin 1 vs. Olin 4	.199	99.44
Olin 1 vs. Olin 5	.051	99.95
Olin 3 vs. Olin 4	.149	99.65
Olin 3 vs. Olin 5	.017	99.99
Olin 4 vs. Olin 5	.157	99.66
Remington 1 vs. Remington 5	.163	99.93
Rio 1 vs. Rio 3	.131	99.96
Rio 1 vs. Rio 4	.171	99.95
Rio 3 vs. Rio 4	.082	99.97
Super-Vel 1 vs. Super-Vel 4	.099	99.78
Super-Vel 1 vs. Super-Vel 5	.150	99.45
Super-Vel 4 vs. Super-Vel 5	.126	99.68

as to the similarity of two bullets. The cut-off values seen for the subject population are not immutable, and would be expected to change as more bullets are added to the database. Given a sufficient database, derived data could be a useful tool in establishing the “rarity” or “commonality” of a specific elemental signature, and the probability of a random match could be estimated. For example, within the small data base used in this study, bullets that had a correlation of 96 or better came from the same box, and only two of the 1650 between-manufacturer comparisons (0.1%) correlated better than 90. This data suggests that when two element signatures match, it is unlikely that the bullets originated from different sources. The extent of each particular source (i.e., the number of identical boxes by each manufacturer) and the bullets available in a particular geographic area at a particular time are all unknown factors. As a result, bullet lead analysis, while clearly more definitive than class characteristics, does not generate individualizing information. However, when the evidence involves multiple bullets whose elemental signatures match multiple signatures from a box, the evidence takes on a higher degree of individualizing character.

Acknowledgment

I would like to acknowledge Mike McNamee for his assistance in sample preparation and running the ICPMS.

References

1. Brunelle RL, Hoffman CM, Snow KB. Comparison of elemental composition of pistol bullets by atomic absorption: preliminary study. *J AOAC* 1970;53:470–4.

2. Blacklock EC, Sadler PA. Shot-gun pellet identification and discrimination. *For Sci Int* 1978;12:109–17.
3. Kramer GW. Determination of antimony in lead-antimony alloys by atomic absorption spectroscopy using indium as an internal standard. *Appl Spec* 1979;33:468–70.
4. Krishnan SS. Trace element analysis by atomic absorption spectrometry and neutron activation analysis in the investigation of shooting cases. *Can Soc Foren Sci J* 1973;6:55–77.
5. Gillespie KA, Krishnan SS. Analysis of lead shot—a comparison of analyses using atomic absorption spectrophotometry and neutron activation analysis. *Can Soc Foren Sci J* 1969;2:95–103.
6. Lukens HR, Schlesinger HL, Guinn VP, Hackleman RP. Forensic neutron activation analysis of bullet-lead specimens. *US Atomic Energy Report GA-10141*, 1970.
7. Lukens HR, Guinn VP. Comparison of bullet lead specimens by nondestructive neutron activation analysis. *J Forensic Sci* 1971;16:301–8.
8. Guy RD, Pate BD. Studies of the trace element content of bullet lead and jacket material. *J Radioanal Chem* 1973;15:135–42.
9. Guinn VP, Purcell MA. A very rapid instrumental neutron activation analysis method for the forensic comparison of bullet-lead specimens. *J Radioanal Chem* 1977;39:85–91.
10. Guinn VP. NAA of bullet-lead evidence specimens in criminal cases. *J Radioanal Chem* 1982;72:645–63.
11. Brandone A, Piancone GF. Characterisation of firearms and bullets by instrumental neutron activation analysis. *Int J Appl Radiat Isot* 1984;35:359–64.
12. Haney MA, Gallagher JF. Elemental analysis of bullet lead by spark source mass spectrometry. *Anal Chem* 1975;47:62–5.
13. Haney MA, Gallagher JF. Differentiation of bullets by spark source mass spectrometry. *J Forensic Sci* 1975;20:484–500.
14. Peters CA, Havekost DG. Multielement analysis of bullet lead by inductively coupled plasma-atomic emission spectrometry. *Crime Lab Digest* 1988;15:33–8.
15. Schmitt TJ, Walters JP, Wynn DA. Analysis of pure lead and lead alloys for the automotive lead/acid battery industry by inductively coupled argon plasma emission spectroscopy. *Appl Spec* 1989;43:687–96.
16. Peele ER, Havekost DG, Peters CA, Riley JP, Halberstam RC. Comparison of bullets using the elemental composition of the lead content. In: *Proceedings of the international symposium on the forensic aspects of trace evidence*; 1991 Je 24–28; Quantico (VA). Washington, DC: USDOJ, (ISBN 0-932115-12-8) 1991;57–68.
17. Suzuki Y, Marumo Y. Determination of trace impurities in lead shotgun pellets by ICP-MS. *Anal Sci* 1996;12:129–32.
18. Dufosse T, Tournon P. Comparison of bullet alloys by chemical analysis: use of ICP-MS method. *Forensic Sci International* 1998;91:197–206.
19. Jarvis KE, Gray AL, Houk RS. *Inductively coupled plasma mass spectrometry*. London: Blackie & Son 1992.
20. Kowalski BR. *Chemometrics: mathematics and statistics in chemistry*. Dordrecht: D. Reidel 1983.
21. Keto RO. Comparison of smokeless powders by pyrolysis capillary gas chromatography and pattern recognition. *J Forensic Sci* 1989;34:74–82.
22. Morgan ML, Walla MD, Rodgers JC. Measuring and displaying chromatographic similarity using cluster analysis. *Chromatography* 1987 July;2(6):12–20.

Additional information and reprint requests:

Raymond O. Keto, BS, MFS
Forensic Chemist
National Laboratory Center
Bureau of Alcohol, Tobacco, and Firearms
Rockville, MD 20850