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A metallurgical review of the interpretation of bullet lead compositional analysis

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Abstract

Comparison of the minor and trace element compositions of bullet lead alloys has been used by some forensic examiners to make definitive positive associations between bullets or lead fragments at a crime scene and samples of bullets linked to a suspect(s). Such conclusions have been based on the elemental analysis of isolated groups of bullets with no consideration of the metallurgical processes involved in the production and refining of the bullet lead alloys. An understanding of the metallurgy of lead refining reveals that the elements quantified in the forensic analysis are carefully controlled in the refining process and that there are logical reasons why some elements are more discriminatory than others. Data for lead alloys supplied to two major ammunition manufacturers confirm that multiple indistinguishable shipments of lead alloys from secondary lead refiners to the ammunition manufacturers are made each year and over a period of many years. The data also demonstrate that distinguishable compositions can come from the same melt or "source" of lead alloy. These results clearly indicate that bullets with indistinguishable compositions could have come from different lead "sources" produced in the same or different years. Furthermore, the observation that two bullets have a distinguishable composition does not necessarily mean that they came from a different "source".

Our results show that the forensic examiner using a method of bullet lead alloy elemental analysis, which quantifies up to six elements is restricted to concluding only that indistinguishable bullets might have come from the same "source," not that they did come from the same "source". In addition, it is quite possible that multiple bullets with similar but distinguishable compositions could have come from the same "source". The authors therefore feel that there is no scientific validity to any conclusions more positive than attributing the possible association as to molten source among bullets from different samples. An understanding of the metallurgical principles operative in the melting/casting process as well as the data acquired for this study, indicate that any forensic conclusions which associate unknown bullets with the "same source", and/or "same box" should fail most or all Daubert criteria.

Keywords: Forensic science; Elemental analysis; Bullet; Lead; Metallurgy

1. Introduction

Two methods are commonly used to compare bullets or bullet fragments found at a crime scene with bullets in the actual or constructive possession of a suspect. The first and most common method uses a non-destructive examination of the bullets to compare various physical features such as dimensions, shape, distinctive markings, and weight. For individual characteristics, optical microscopy can be used to compare striations on the crime scene bullets or fragments with those from another event(s) and/or with bullets from a known source, such as a firearm owned by a suspect [1,2,3]. The striations used for this comparison result from forced contact of the bullet with rifling features (lands and grooves)

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during travel of the bullet through the barrel. This information can be used by a firearms examiner as a basis for a conclusion as to whether or not there is a positive association [4,5]. Another method in use for comparing questioned and known bullets involves a comparison of the chemical compositions of the lead alloys comprising the bullets [6,7,8,9]. For the purposes of this paper, we shall call this general method elemental analysis comparison (EAC).

In EAC, the major, minor, and trace compositional elements are identified, quantified, and compared. Various analytical techniques, including neutron activation analysis (NAA), [6,10–13] spark source mass spectroscopy (SSMS), [14] inductively coupled plasma atomic emission spectroscopy (ICP–AES) or as it is now known, inductively coupled plasma optical emission spectroscopy (ICP–OES), [7,8] atomic absorption spectroscopy (AAS), [15] and inductively coupled plasma mass spectroscopy (ICP–MS) [9] have been used to determine the chemical composition of bullets and bullet fragments. (Another common analytical technique used by the lead industry for compositional analysis is spark discharge or spark source optical emission spectroscopy (SS–OES).) The number of elements measured has been observed to range from three to twenty, but the current method used by one major law enforcement laboratory in the USA quantifies six elements with ICP–OES [7,8]: antimony, tin, arsenic, copper, bismuth, and silver. Another laboratory quantifies eight elements with ICP–MS: antimony, tin, arsenic, copper, bismuth, silver, tellurium and cadmium [9]. The bullets and/or fragments to be compared are then separated into groups by a method that results in each group having members with an indistinguishable elemental signature or pattern within the precision of the measurement technique used for the analysis. The specimen(s) of each group must have the same amount of each and every element analyzed using, for example, a two standard deviation criterion for the grouping. There may be a single group found for all of the bullets or there may be more. The identifying signature(s) formed by the combination of the quantified amounts of these elements in the lead alloy from the crime scene bullets or groups of crime scene bullets is compared to the signature(s) from the groups of bullets from a suspect. If the signatures are distinguishable, by the example method or some other form of valid statistical analysis, then this result has been interpreted as being inconsistent with the bullets associated with the suspect being associated with the crime scene. If the signatures of one or more groups from the crime scene are indistinguishable from one or more groups from bullets under a suspect's actual or constructive control, however, then the evidence has been interpreted as being consistent with the association of the suspect with the crime scene. In fact, in criminal cases, the United States Federal Bureau of Investigation (FBI) expert witnesses have presented testimony such as "Bullets with the same composition, that is, compositions that are analytically indistinguishable typically come from the same box of cartridges [16]", and, (when comparing the indistinguishable groups of crime scene bullet fragments with bullets in the suspect's control) "It's my opinion that all of those bullets come from the same box [16]". Sometimes the testimony has been modified to indicate that the bullets were "manufactured on or about the same day," [16,17] or that bullets in the same box were "...made at the same time, exactly the same time [18]".

It is testimony such as this that aroused the interest of the authors, who are metallurgists and analytical chemists, to ascertain whether such statements are in general valid. At the outset of our research, it became clear that what was being said in courts of law was quite different that what has been published in the forensic science literature. It also became clear that there has never been a well-designed study to examine bullet production for a significant length of time to determine whether bullet lead compositional analysis was even meaningful. Such a study would, of necessity, either examine production on a continuous (for example daily) basis or with a well-designed sampling schedule for a sufficient period of time to ascertain the likelihood of finding the same compositions in different boxes assembled on different days or in different years.

We note that Keto [9] has concluded from his study of a small number of bullets that in general bullet lead analysis does not generate individualizing information. However other forensic examiners have continued to conclude that positive associations can be made between bullets associated with a suspect and those from a crime scene. The only published rationale purported to provide a foundation for these conclusions is that "if two bullets are produced from the same homogeneous source of lead, then they will have analytically indistinguishable composition [7]". Also, "two bullets must be analytically indistinguishable in all measured elements before they can be attributed to a common source [7]". Such hypothetical statements would appear to be obvious, even to the casual observer, but neither statement is necessarily true for bullet manufacturing. Furthermore, the word "source," has never been given a clear definition. As indicated in court transcripts, laboratory reports and published articles, it either refers to a specific lot or shipment of lead alloy to an ammunition manufacturer which originated from the same casting (melt) or pour of that alloy at the lead refiner; or it refers to the lead from any remelting operation done at the bullet manufacturer. The later operation is a continuous or semi-continuous process so that there is really no individualized "source" at the bullet manufacturer that can be uniquely identified. We also note that in the limited study by Peele et. al. [7], which included only 16 boxes of ammunition (800 rounds), they found indistinguishable composition groups in boxes produced 7 months apart for Winchester ammunition and 15 months apart for Federal ammunition. The research and investigation conducted by, and the professional knowledge and experiences of, the authors, therefore question the validity of using the two above-referenced statements to provide any type of foundation for positive associations among bullet lead samples by EAC.

The meaningful forensic questions to be addressed should be: (1) "If the compositions of two or more bullets are indistinguishable, were they, in fact, produced from the same molten source of lead?" This, of course, begs the question, "How unique is each source of lead?", and (2) "Is each such 'source of lead' sufficiently homogenous to justify use of EAC as it is applied today?" Certainly, if an ammunition manufacturer used multiple "lead sources" each year that were compositionally indistinguishable by the EAC method, then the method could not positively associate bullets from a suspect with a crime scene and it would be of limited value in establishing even that the data is anything more than possibly consistent with two bullets coming from the same "source". Also, if each "source" of lead were not perfectly homogeneous, then two or more bullets with distinguishable compositions could have derived from the same "source". Thus if two bullets were found to have slightly differing but distinguishable compositions, could they have in fact some from the same "source"? We present data from several years of lead alloy production for the ammunition community that demonstrates that positive associations are without foundation and that distinguishable bullets could very likely have come from the same "source".

It is important to examine and understand the terms homogeneous (as used in describing the absence of compositional variation in a single source of lead) and analytically indistinguishable (as used in describing compositional comparisons) in relation to the lead alloys used for the production of bullets. To make inferences and render positive conclusions as to association, it is also important to determine how unique each "source of lead" actually is. Since, according to industry data that we use as exemplars, there may be as many as 20–30 lots (at 20–100 tonnes per lot, for a shipment range of 400,000–3,000,000 kg) of lead shipped to a single major ammunition manufacturer each year for 0.22 caliber bullet production, and considering that chemical composition specifications do not change frequently, the forensic scientist needs to establish whether multiple lots are really always distinguishable by EAC and hence unique. Previous investigators have studied only a very limited number of bullets from assembled boxes of ammunition, but we found no work or publication which established that there are in fact unique and/or homogeneous lead "sources". Such characterizations are essential premises to the application of the EAC method as it has been presented in the courtroom for positive associations as to "common source of molten lead".

We present this article in two sections. The first section is a basic discussion of lead smelting or refining for the forensic scientist who may not be fully aware of the lead refining process and the quality control that is used to assure acceptable compositions of the product. The second section presents compositional data for several 2-year segments of production of bullet lead alloys from two major lead smelters supplying several major US ammunition manufacturers. Compositional data for lead alloys used in the production of 0.22 caliber bullets by two major US manufacturers of ammunition for several 2-year periods of production approximately 13 years apart (1987–1988 and 1998–2000) are herein presented and discussed. The alloy chosen for this study is also regularly used for the production of other calibers of bullets by the bullet manufacturers. For the sake of simplicity we will only discuss it in terms of 0.22 caliber ammunition.

2. Lead refining

To aid the reader in understanding EAC, the metallurgical methods used in recycling and refining lead alloys will be discussed briefly. The elemental composition of each lot of lead alloy is primarily determined during the lead-refining step and not during the bullet-forming processes at the ammunition manufacturer. This fact alone reveals why visits to bullet manufacturers is of little significant benefit in, and provides no scientific foundation for, rendering conclusions relating to "common source(s)" of lead. An understanding of the metallurgical principles and practices of lead refining for the manufacture of bullets also shows that the elemental analytes used in present EAC practice are not generally independent variables. In fact, addition, removal, and/or control of these elements are the primary reasons for refining, and there are simple, logical reasons, due in large part to metallurgical processes, why previous investigators have found some of these elements to be "more discriminating" than others. More 0.22 caliber rim-fire ammunition is produced in the USA each year than any other caliber of ammunition, and the use of 0.22 caliber firearms in the commission of felonies is not uncommon [19]. For these reasons, and since the commercial manufacture of 0.22 caliber lead bullets is typical of the manufacturing practices for other calibers of lead bullets, 0.22 caliber practices were studied as the example for discussion of bullet manufacture and the EAC method.

Most 0.22 caliber bullets are made with a lead-antimony alloy specified to contain 0–1.5 wt.% antimony. The two popular alloys that we consider contain a nominal 0.7 and 0.75% antimony and are referred to as alloy 1 and alloy 2, respectively, in this paper. Both of these lead alloys are supplied to two different major US ammunition manufacturers by secondary lead refiners (or lead recyclers) in the USA As antimony is the only alloying addition, antimony content is typically specified by an ammunition manufacturer to be within a certain range. For example, the antimony content of one of the alloys we discuss is acceptable to one major bullet manufacturer in the range of 0.6–0.8% antimony, and the other alloy is acceptable to another major bullet manufacturer in the range of 0.6–1.1% antimony. Undesirable elements are specified only to be less than a certain maximum value. The minor and trace elements tin, copper, and arsenic are typically specified to be 0.15% maximum, 0.10% maximum, and 0.10% maximum,

respectively. For 0.22 caliber bullets, bismuth is generally not specified and silver may or may not be specified. Lead is generally supplied by the lead refiner to the ammunition manufacturer in the form of cast ingots or pigs weighing about 30–60 kg each or as cylindrical billets sized ready for insertion into a bullet wire extruder. Each lot or batch of lead is typically 20,000–100,000 kg in size, and each individual lot or batch can be the lead "source" to which previous investigators have alluded [6,7].

Lead is unusual among the common industrial metals in that it can be recycled very effectively [20]. Most of the lead products in use today come from recycled or secondary lead. The main source of raw material for secondary lead smelters is spent lead-acid batteries. Primary lead, smelted from lead ores, is used to make up the difference between the overall consumer demand for lead and the current secondary lead supply. The smelting and refining of secondary lead are quite similar to the processes used for primary lead, but generally there are fewer steps involved [20–24]. Once relatively pure lead (called lead bullion) is produced, the necessary alloying elements are added to meet the requirements of the bullet manufacturer. In the 0.22 caliber ammunition lead alloy under discussion, there is only one alloying element, antimony, that is added as specified. The important processing steps that ultimately control the presence and amount of both alloying and impurity elements (including antimony, arsenic, tin, copper, bismuth, and silver) occur in the refining stage. Keep in mind that the ammunition community utilizes less that 5% of the refined lead produced each year. The quality control used in the lead industry is therefore primarily determined by the needs of the battery community.

The initial smelting and refining of secondary lead is generally done in a blast furnace, rotary furnace or reverberatory furnace. Each of these has specific economic and performance characteristics which produce different qualities of lead bullion [22]. They may be used in conjunction with each other or alone, and the output from each may be blended to obtain a desired product in an efficient manner. The process of refining (the removal of unwanted impurities) occurs in these furnaces or can be done as a separate operation in individual kettles.

A process known as copper drossing generally accomplishes the removal of substantially all the copper. This is a simple cooling process in a large kettle (containing up to 350 tonnes of bullion at some refiners) in which impurity compounds (mostly antimonides, arsenides, and stannides) separate as either solid or immiscible liquid phases due to the decreasing solubility of the phases with lower temperatures. The impurities are removed by skimming during cooling, and the melt is finally cooled to about 340 °C, just above the freezing point of lead. To remove the last of the copper (to the 20–200 ppm range), sulfur or sulfur-containing compounds may be stirred into the melt, and cooling is continued to very near the freezing point of the melt (~330 °C). This is called sulfur drossing. Compounds other than those of copper also come out during drossing, primarily high melting point compounds of iron and zinc, followed by antimonides, arsenides, and, at lower temperatures, various sulphides. The phases to be removed float on the lead surface and are called mattes and speiss, depending on the impurities they contain. They are skimmed off, tapped off, or otherwise removed.

At this point antimony, arsenic, tin, bismuth, and any noble metals (primarily silver) are the major impurities remaining (at this stage of the process, antimony is not an alloying addition). The first three of these elements are removed in an oxidation process called softening (so named because the removal of these hardening elements softens the lead bullion). Softening depends on the fact that these elements are more readily oxidized than lead under most molten conditions, and it can be accomplished by several methods. The melt can be heated to 700–800 °C in a reverberatory furnace and agitated with air or steam. An oxide slag, containing some lead and most of the antimony, arsenic, and tin forms and can be skimmed off. If a kettle is used, the softening can be done at a lower temperature, and sodium nitrate can be used to form the slag. The impurities removed are in the form of sodium arsenates, antimonates, and stannates. Bismuth and silver are not removed in the softening process.

Bismuth oxidizes less readily than lead and must be removed, if necessary, by a separate process involving electrolysis or the Kroll–Betterton process. If bismuth levels are low enough in the recycled material, this step is not necessary. In general, secondary lead smelters do not remove bismuth. Blending of lead bullions may also be used to accomplish desired bismuth levels. The step to remove bismuth is done only if the specifications require it, since it is an added expense.

Silver is removed last and is generally removed only in primary lead refining. Desilvering can be done by successive cooling and crystallization steps and/or by the Parkes process. In the latter process, Zn is stirred into the melt that is then cooled. A separate zinc-rich phase containing the silver, any gold, and some lead separates to the top and is removed. The zinc remaining in the melt is then removed by an oxidation or a vacuum dezincing (distillation) process. At this point, the bullion is relatively pure lead and is ready for alloying. Again, secondary lead smelters do not remove silver unless necessary or economically desirable. Silver and bismuth levels in secondary metal are essentially controlled by the specification limits set by the battery companies, since spent batteries are the largest source of raw material for the secondary smelters. Normally in secondary smelters, adjustments to silver and bismuth are not required to meet bullet alloy specifications.

An important point to note here is that, at this point in the process, the elements antimony, arsenic, tin, copper, bismuth, and silver that are analyzed in the EAC method are intentionally controlled impurity elements in the lead bullion and in the final alloy. They are removed to less than the maximum allowable levels required either by specification, by economic considerations, or are controlled by the

concentrations in the available raw material when the secondary refiner does not adjust their compositions. Moreover, the impurity elements tend to remain within rather narrow composition ranges that are determined by the specific refining processes used at the smelter. Also, the antimony, arsenic, and tin are removed in the same preferential oxidation process; consequently, the amounts of each tend to track each other during the refining process, all other things being equal.

If soft or unalloyed lead, such as is commonly used in jacketed bullets, is desired then the refined lead bullion is cast as refined. When a lead alloy is desired, the necessary alloying element(s) is added as needed prior to casting the material. In our example, antimony is added in the amount of approximately 0.7wt.%. The antimony can be added as blast furnace bullion, which contains relatively high levels of antimony, arsenic, and tin, pure or impure antimony metal or both. Whatever method is used, it is economically optimized and may not change over long periods of time. The final overall composition of the lot of lead is checked by chemical analysis and, if acceptable, casting begins. The casting is done from a large kettle, and since each lot consists of 20,000–100,000 kg of lead, it can take longer than eight hours to complete. The lead is cast into ingots, commonly called pigs, which generally weigh about 30 kg. Variability in composition of the pigs occurs from the beginning to end of the pour because of continual oxidation of the melt surface and stratification of impurities in the kettle over the time of the pour. This can change the overall composition of the pigs as the pour proceeds because elements such as antimony, tin, and arsenic oxidize more rapidly than lead and become preferentially depleted from the melt as the casting continues.

The above description is general and includes procedures used at both primary and secondary smelters. To further illustrate actual secondary lead refining practice, we shall now consider a general (i.e., non-proprietary) description of the two specific secondary lead refining processes used to produce alloy 1 (0.7% antimony) and alloy 2 (0.75% antimony). A specific description of the process for alloy 1 is for a secondary smelter having both reverberatory and blast furnaces and begins by separating the lead bearing materials in a battery from the case material and the acid. The lead bearing materials are normally initially smelted in a reverberatory furnace. The reverberatory furnace is an oxidizing furnace and most of the antimony, arsenic and tin are removed in a slag, which floats on the molten lead. The molten lead bullion in the reverberatory furnace is tapped off to be further refined. Almost all of the noble metals (primarily silver) are contained in the lead bullion. The molten slag is also tapped from the reverberatory furnace and is smelted in the blast furnace. The blast furnace is a reducing furnace and the oxidized metals in the reverberatory slag are reduced to their metallic components. The reduced metal is tapped from the furnace and can be mixed with reverberatory bullion before being further refined in large kettles.

The production of the bullet alloy begins by mixing blast and reverberatory bullion in a large kettle. The amount of blast metal used is controlled by its antimony:tin:arsenic ratio. The normal ratio is such that the maximum tin level is reached before there is sufficient antimony in the mix. The arsenic level in the blast metal is such that the arsenic specification maximum is not exceeded. The antimony is adjusted later in the refining steps by adding pure antimony metal. An alternate strategy is to "charge for antimony". In this strategy sufficient blast metal is added to get the antimony within specification. If the tin and/or the arsenic are above the specification limits then they are removed using air oxidation and/or chemical refining methods. The mixing of these two bullions at 370–430 °C causes dross to form on the surface of the melt. The dross contains metallic oxides mixed with molten alloyed metal and is known as a "wet" dross. The molten metal part of the dross is separated from the oxides or "dried" using tar, sawdust, or other chemicals. This "dried" dross is then skimmed off of the surface of the melt. If tin and arsenic removal is necessary the pot is adjusted to 450–550 °C and air oxidation and/or chemical refining methods are used. The pot is cooled to just above the freezing point of the melt and sulfur and iron pyrite are mixed in to remove copper to below the specification limits. The dross formed by the sulfur and iron pyrite is skimmed from the kettle and the temperature is adjusted to 430–460 °C. If necessary, the antimony level is adjusted using pure antimony metal. Caustic (solid sodium hydroxide) is added to remove oxides and drosses from the melt. Remaining refining chemicals are removed using sawdust and charcoal. A final analysis is conducted to assure that all specifications are met, and the kettle is cast into 30–35 kg "pigs". The pigs are stamped with a lot number and alloy designation. This procedure seldom requires change due to the uniform feed material to the smelter and to the uniform furnace operation. Metal produced by this procedure may contain tin and arsenic because of the blast metal used to supply some of the antimony required to meet the final antimony specification. The process is monitored by periodic analysis of the lead using SS–OES. The refining process is usually accomplished in 1–3 days and over the course of the process the lead may be analyzed 20 or more times for 17 elements.

Alloy 2 is refined from blast furnace lead only. The alloy is refined in a kettle with a 115,000 kg capacity. The starting material contains all of the elements used in the EAC analysis as well as several others. The first (proprietary) refining step for alloy 2 removes copper as well as some other impurities. The specification for alloy 2 requires copper to be 0.08% maximum. The proprietary procedure usually lowers it to 0.02% or less. Tin and arsenic are removed next by a high temperature oxidation process with agitation followed by caustic soda and caustic potash treatments. The impurities are removed by skimming them off the top of the molten lead. Some antimony is generally lost in this refining step since it oxidizes along with tin and arsenic.

Pure metallic antimony is added as needed to raise the antimony content to the required amount. Charcoal is used to remove any chemical residues. There is no attempt made to adjust the concentrations of bismuth or silver. The finished lead alloy product is cast into 30 kg pigs or billets. The pigs are usually remelted into billets for use at the ammunition manufacturer. When in the form of billets, the lead is not remelted by the ammunition manufacturer. A typical lot size for alloy 2 is 98,000 kg.

Variability in composition within each individual pig is also caused by a phenomenon known as segregation that occurs during solidification of the pig. As the cast pig cools, it solidifies first at the (cooler) exterior surface. The center of the pig is the last region to solidify. Impurity elements that are more soluble in the liquid phase than the growing solid phase are rejected into the liquid phase and hence become more concentrated at the center of the pig. Because of the nature of the various binary elemental phase diagrams (the slope and position of the liquidus boundary) and depending on the amounts of each element present in the alloy, this phenomenon is expected to be more pronounced for elements like antimony, to have only a minor effect for elements like Bi, and to have little effect on elements that are present at the less than 10 ppm level such as tin and arsenic in alloy 2. The effects for the other elements of interest would strongly depend on the amounts present and on cooling rates. Segregation thus increases the lack of homogeneity in each individual pig. This is a basic metallurgical phenomenon and tendency known to exist in all casting processes. Note, also, that differences in cooling rate alone can result in significantly different compositions from the surface of the pig to the center, and between samples taken from two different pigs of identical, overall (average) composition.

3. Basic 0.22 caliber bullet fabrication

The refined lead alloy is commonly shipped to the bullet manufacturer in pig form or as cylindrical billets. If shipped as pigs, the pigs are remelted and cast into cylindrical billets suitable for insertion into wire extruders. If shipped as billets, the billets are inserted directly in to the wire extruder. In the extrusion process, the lead is forced through a small cylindrical die to form wire with a diameter of slightly less than 0.22 inch. This process is analogous to squeezing toothpaste from a toothpaste tube except that much higher pressures are used, since lead wire is not as soft as toothpaste. The lead wire is or can be wound on spools or wound into storage drums from where it can be processed, transported, or stored for later use. The wire then proceeds to a cutter where appropriate lengths or slugs of wire are cut to result in a final bullet weight of about 40 grains (2.59 g). Each slug of lead wire is then formed (upset forged, swaged, etc.) to give the bullet its final shape and physical features. The bullets are lubricated during processing and coated with a wax-like organic to prevent oxidation during storage. In final assembly, each bullet is fixed to a brass cartridge case that contains the powder and primer material. The finished product is typically then put into boxes of 50 cartridges each and assembled into "bricks," or 10-box assemblies, of ammunition. Containers of 100 or more cartridges are also commonly used.

Most of the processes in the actual manufacture of the final 0.22 caliber product are physical manipulations of the lead alloy material and do not affect the composition of the alloy [25]. The only process at the ammunition manufacturer that might change the composition of the alloy is the remelting of the pigs, if it occurs, in order to provide a properly sized extrusion billet for the wire extruder prior to the extrusion of the lead wire. Melting in air results in oxidation of the melt surface and, as mentioned, the chemical components of the melt (i.e. the lead, antimony, tin, etc.) oxidize at different rates. Melting at this stage is most likely to increase variability of the final product lots, but it will generally not increase homogeneity of the lead alloy lot, since it is not a controlled refining process. It most likely results in a general loss of the elements antimony, arsenic, and tin relative to lead, since these oxidize more readily than lead and will be lost at a more rapid rate if the alloy is air melted. During this remelting process, segregation of the major alloying element(s) as well as minor and trace elements can occur. The remelting process at the bullet manufacturer involves melting a much smaller amount of the alloy than the smelter lot size. Typically a kettle of about 5000 kg or smaller is used and it is a continuous or semi-continuous process with a constant addition of pigs to maintain a certain level of molten material in the kettle. Another factor to consider is that partial shipments of the same lot of lead form the lead smelter to the ammunition plant do occur and lead from the same lead lot may be shipped at separate times. The smelter may also have an inventory of several lots of the alloy, and since each lot constitutes several truckloads, the lots may not be delivered contiguously to the ammunition manufacturer, and so different lots can become mixed in various proportions at the ammunition plant. Even the physical extrusion process itself can contribute to non-homogeneity of the product. These phenomena have been well documented for lead and lead alloys which are extruded for underground cable sheathing used in the electrical cable sheathing industry [26,27].

4. Lead alloy data

Elemental composition data of the lead alloys supplied to two major ammunition manufacturers are listed in Table 1 through 4. Tables 1 and 2 contain data for 28 lots of a nominal 0.7 wt.% alloy supplied to the first ammunition manufacturer by a nearby secondary lead smelter for a 15-month period (January 1999–March 2000). Unfortunately, there is a 5 months time gap in 1999 for which we were unable to obtain data. Table 1 lists the data actually measured

Table 1
Variability of lot composition for 0.22 caliber alloy no. 1 (1999–2000)

Date	Lot no.	Time of sample	Sb (%)	Sn (ppm)	Cu (ppm)	As (ppm)	Bi (ppm)	Ag (ppm)
11 January 1999	423	B	0.673	100	207	194	100	25
		M	0.678	106	244	195	99	26
		E	0.680	74	247	196	100	27
18 January 1999	424	B	0.710	414	169	110	92	24
		M	0.710	414	172	112	93	24
		E	0.636	21	181	82	93	24
3 February 1999	424A	B	0.711	153	119	129	96	30
		M	0.714	139	121	130	96	31
		E	0.711	129	121	127	96	30
3 February 1999	426	B	0.718	537	222	151	98	26
		M	0.725	522	202	147	98	26
		E	0.738	541	179	151	99	27
10 February 1999	427	B	0.671	18	144	68	99	31
		M	0.665	12	144	70	98	30
		E	0.663	13	144	69	98	30
22 February 1999	429	B	0.747	1156	86	236	96	54
		M	0.746	1128	87	233	97	54
		E	0.743	1071	87	231	97	54
2 August 1999	444	B	0.744	194	206	130	102	28
		M	0.730	138	206	132	102	28
		E	0.722	117	198	126	102	27
18 August 1999	445	B	0.674	190	173	239	103	28
		M	0.667	178	174	235	102	28
		E	0.665	152	174	235	102	28
10 September 1999	446	B	0.707	118	207	112	107	35
		M	0.706	117	214	114	107	35
		E	0.696	97	198	111	107	34
22 September 1999	447	B	0.704	154	181	62	110	33
		M	0.715	136	187	63	111	34
		E	0.710	152	177	62	110	34
1 October 1999	448	B	0.733	266	49	210	102	29
		M	0.735	297	43	219	102	29
		E	0.725	268	44	214	102	29
12 October 1999	450	B	0.687	253	135	83	106	31
		M	0.694	234	137	82	105	32
		E	0.692	258	137	83	106	32
15 November 1999	451	B	0.680	51	79	103	109	41
		M	0.681	26	81	103	110	42
		E	0.684	17	83	102	111	43
22 November 1999	452	B	0.697	109	28	62	98	35
		M	0.699	104	29	62	99	35
		E	0.700	101	29	62	98	35
8 December 1999	453	B	0.705	5	135	116	99	36
		M	0.706	<1	129	113	94	37
		E	0.668	<1	129	102	93	36
8 December 1999	454[a]	B	0.747	377	250	139	97	34
		M	0.753	367	263	140	97	36
		E	0.718	45	156	121	95	36

Table 1 (*Continued*)

Date	Lot no.	Time of sample	Sb (%)	Sn (ppm)	Cu (ppm)	As (ppm)	Bi (ppm)	Ag (ppm)
15 December 1999	455	B	0.669	382	214	142	94	29
		M	0.666	374	207	138	93	29
		E	0.673	369	208	142	94	29
17 December 1999	456	B	0.682	348	200	127	94	31
		M	0.676	336	185	122	94	30
		E	0.681	294	185	125	95	30
27 December 1999	456A	B	0.738	125	139	244	104	36
		M	0.741	89	137	248	104	36
		E	0.735	82	137	249	104	36
5 January 2000	457	B	0.672	210	140	142	103	30
		M	0.674	188	140	144	103	31
		E	0.666	141	139	138	103	31
12 January 2000	459	B	0.739	618	19	343	104	33
		M	0.743	623	20	357	104	33
		E	0.740	608	21	355	105	34
12 January 2000	460[b]	B	0.694	625	12	224	102	33
		M	0.697	586	12	223	102	33
		E	0.724	602	16	292	103	33
25 January 2000	461	B	0.730	693	51	207	96	33
		M	0.680	661	51	195	98	34
		E	0.679	665	52	196	97	34
14 February 2000	463	B	0.744	681	2	181	99	33
		M	0.740	678	1	174	99	33
		E	0.743	678	1	175	99	33
21 February 2000	464	B	0.682	730	34	160	101	32
		M	0.679	718	33	162	100	32
		E	0.678	391	80	136	102	33
21 February 2000	465[c]	B	0.681	392	81	137	102	33
		M	0.680	221	104	123	102	33
		E	0.662	212	103	117	102	32
1 March 2000	466	B	0.722	666	67	210	100	35
		M	0.716	619	64	205	100	34
		E	0.725	611	66	206	101	35
2 March 2000	467	B	0.709	474	91	183	101	35
		M	0.706	467	93	180	101	34
		E	0.700	447	94	178	101	34

[a] Piggybacked with lot no. 453 B = beginning, M = mid, E = end.
[b] Piggybacked with lot no. 459.
[c] Piggybacked with lot no. 464.

at the time of the pour, where samples and data are taken at the beginning, middle and end of the casting process. Table 2 contains the average compositions of the lots as computed from Table 1. Table 3 contains data for 63 lots of a nominal 0.75 wt.% alloy supplied to a second ammunition manufacturer by another secondary lead smelter for a 24-month period (May 1998–May 2000). Table 4 contains data for 31 lots of the same 0.75% alloy for a 13-month time period 12 years earlier (August 1987–October 1988). Although, for quality control reasons, 15 or more elements for each lot of an alloy are measured by each smelter, we list only six elements for a direct comparison with most of the past published bullet lead information: antimony, tin, copper, arsenic, bismuth, and silver. Both smelters measure the composition at the beginning and end of each pour or casting from the kettle, and the first smelter additionally measures the composition at the midpoint of each pour as well. Samples are taken at the outlet tap of the casting kettle to get an accurate representation of the pig or billet being cast at the time of sampling. One smelter uses SS–OES and the other has used both ICP–OES and SS–OES analysis to quantify compositions. All of the data shown was acquired

Table 2
Average lot composition for 0.22 caliber alloy no. 1 (wt.%) (1999–2000)

Date	Lot no.	Sb (%)	Sn (ppm)	Cu (ppm)	As (ppm)	Bi (ppm)	Ag (ppm)
11 January 1999	423	0.6770	93	233	195	100	26
18 January 1999	424	0.6850	280	170	100	93	24
3 February 1999	424A	0.7120	140	120	130	96	30
2 February 1999	426	0.7170	533	201	149	98	26
10 February 1999	427	0.6660	14	140	69	98	30
22 February 1999	429	0.7450	1120	87	233	97	54
2 August 1999	444	0.7320	149	203	129	102	27
18 August 1999	445	0.6680	170	170	240	102	28
10 September 1999	446	0.7030	111	206	112	107	35
22 September 1999	447	0.7100	147	182	62	110	34
1 October 1999	448	0.7310	280	45	210	102	29
12 October 1999	450	0.6910	248	136	83	106	32
15 November 1999	451	0.6820	30	80	100	110	42
22 November 1999	452	0.6990	105	29	62	98	35
8 December 1999	453	0.6930	2	131	110	94	36
8 December 1999	454[a]	0.7390	400	220	130	96	35
15 December 1999	455	0.6690	375	209	140	94	29
17 December 1999	456	0.6800	330	190	125	94	30
27 December 1999	456A	0.7380	100	140	250	104	36
5 January 2000	457	0.6710	180	140	140	103	31
12 January 2000	459	0.7410	616	21	352	104	33
12 January 2000	460[b]	0.7050	604	13	246	102	33
25 January 2000	461	0.6960	669	51	199	97	34
14 February 2000	463	0.7420	680	1	180	99	33
21 February 2000	464	0.6800	610	49	150	101	32
21 February 2000	465[c]	0.6740	280	96	130	102	33
1 March 2000	466	0.7210	632	66	207	100	35
2 March 2000	467	0.7050	463	93	180	101	34

[a] Piggybacked with lot no. 453.
[b] Piggybacked with lot no. 459.
[c] Piggybacked with lot no. 464.

with SS–OES. Both refiners use NIST standard reference material (SRM) numbers C2415, C2416 and C2417 and C2418 as standards. Calibration is performed on a daily basis.

Each lot of lead alloy can vary in total weight depending on the order from the ammunition manufacturer, generally in the range of 30,000–60,000 kg. Thus, each lot represents on the average about 17 million 40 grain bullets, or 340,000 boxes of 0.22 caliber ammunition.

5. Discussion

The use of the EAC method to differentiate among groups of bullets to develop a positive link or possible positive link between different groups of bullets depends upon several assumptions. The first implicit assumption is that each lot (or source) of lead alloy is somehow unique using the six-element "signature" used in the EAC method. If this was not the case, then clearly the bullets in question could have been produced at several (or many) different times by a bullet manufacturer(s). If in fact, it could be shown that the groups of bullets analyzed could have come from a number of or many different lots, it would be more likely that they did not come from the same lot of lead. We contend that the assumption of lot or source uniqueness is not necessarily true because analytically indistinguishable lots are, in fact, produced reasonably often by lead smelters. The second key assumption is that each lot of lead alloy is compositionally uniform (homogeneous) enough to produce a population of bullets such that any statistically valid samples taken from this population are analytically indistinguishable from one another, as determined by the EAC method. Ignoring the metallurgical phenomena of segregation, preferential oxidation, and stratification which are known to occur in large castings, and if sample sizes (the number of samples, not their weight) were sufficiently large, and the population from which the samples come were well characterized, then this assumption might have some merit. However, the appropriate question for the situation under discussion is: does this assumption apply to bullet manufacturing, particularly when each sample from a bullet weighs an infinitesimal fraction of the total pig or billet weight? We contend that the answer in the real world is no because the pigs of lead alloy, and hence

Table 3
Lot composition for 0.22 caliber alloy no. 2 (1998–2000)

Date	Lot no.	Sb (%)	Sn (ppm)	Cu (ppm)	As (ppm)	Bi (ppm)	Ag (ppm)
10 May 1998	447						
	Approval	0.7700	<1	35	3	99	22
	After/cast	0.7700	<1	36	4	100	23
20 May 1998	468						
	Approval	0.7200	<1	80	4	97	25
	After/cast	0.7600	<1	80	3	97	25
24 May 1998	481						
	Approval	0.8100	<1	3	4	100	30
	After/cast	0.7900	<1	3	4	100	32
5 June 1998	515						
	Approval	0.7100	<1	50	3	100	34
	After/cast	0.7200	<1	55	3	100	34
2 July 1998	589						
	Approval	0.7100	<1	50	4	100	30
	After/cast	0.7000	<1	57	5	100	30
7 July 1998	605						
	Approval	0.7300	<1	120	3	100	29
	After/cast	0.7100	<1	130	4	100	29
19 July 1998	645						
	Approval	1.0600	<1	50	3	110	26
	After/cast	1.0300	<1	51	5	110	27
24 July 1998	659						
	Approval	0.7500	<1	25	3	100	29
	After/cast	0.7400	<1	27	4	100	30
5 August 1998	698						
	Approval	0.9100	<1	51	5	100	28
	After/cast	0.8800	<1	51	6	100	28
22 August 1998	750						
	Approval	0.6800	<1	90	5	100	29
	After/cast	0.6700	<1	94	4	100	28
2 September 1998	780						
	Approval	0.8000	<1	90	4	100	30
	After/cast	0.7300	1	94	7	110	31
13 September 1998	811						
	Approval	0.8200	5	45	9	100	29
	After/cast	0.7900	<1	46	8	100	29
16 September 1998	820						
	Approval	0.7300	<1	98	9	100	35
	After/cast	0.6900	<1	95	5	100	34
2 October 1998	866						
	Approval	0.7000	<1	49	7	100	32
	After/cast	0.6900	<1	50	10	100	
2 October 1998	867						
	Approval	0.7000	<1	49	7	100	32
	After/cast	0.6900	<1	50	10	100	
11 October 1998	895						
	Approval	0.9000	<1	160	4	100	30
	After/cast	0.8900	<1	160	5	100	29

Table 3 (*Continued*)

Date	Lot no.	Sb (%)	Sn (ppm)	Cu (ppm)	As (ppm)	Bi (ppm)	Ag (ppm)
26 October 1998	955						
	Approval	0.8100	<1	100	5	100	30
	After/cast	0.7900	<1	100	4	97	29
2 November 1998	978						
	Approval	0.8300	<1	150	5	98	30
	After/cast	0.8500	<1	160	5	100	30
8 November 1998	995						
	Approval	0.6800	<1	190	5	98	29
	After/cast	0.6700	<1	190	5	99	29
1 December 1998	076						
	Approval	0.9100	1	110	6	110	34
	After/cast	0.9100	1	120	5	110	34
12 December 1998	110						
	Approval	0.7900	<1	60	6	100	35
	After/cast	0.7600	<1	60	6	100	33
3 January 1999	192						
	Approval	0.6600	1	87	6	110	01
	After/cast	0.6600	<1	90	6	110	33
16 January 1999	234						
	Approval	0.6800	<1	82	6	110	44
	After/cast	0.6700	<1	82	6	110	44
4 February1999	305						
	Approval	0.7400	1	83	13	110	33
	After/cast	0.7300	1	83	6	100	34
14 February1999	336						
	Approval	1.000	5	31	7	100	30
	After/cast	0.9800	<1	34	8	100	30
19 February1999	349						
	Approval	0.9100	<1	65	3	100	36
	After/cast	0.9000	<1	65	3	100	36
7 March 1999	409						
	Approval	0.8700	7	61	4	110	30
	After/cast	0.8600	6	61	4	110	30
7 March 1999	410						
	Approval	0.8400	1	62	10	100	31
	After/cast	0.8400	1	62	10	100	31
28 March 1999	472						
	Approval	0.6900	<1	120	5	100	29
	After/cast	0.6900	<1	130	4	100	30
3 April 1999	493						
	Approval	0.7200	<1	130	5	110	40
	After/cast	0.7000	<1	130	6	110	41
18 April 1999	542						
	Approval	0.9300	<1	60	4	100	30
	After/cast	0.9200	<1	60	1	110	30
4 May 1999	599						
	Approval	0.8300	<1	66	4	110	33
	After/cast	0.7900	<1	67	4	110	33
14 May 1999	633						
	Approval	0.8500	<1	140	4	110	33
	After/cast	0.8300	<1	140	5	110	34

Table 3 (*Continued*)

Date	Lot no.	Sb (%)	Sn (ppm)	Cu (ppm)	As (ppm)	Bi (ppm)	Ag (ppm)
31 May 1999	686						
	Approval	0.6600	<1	110	40	110	39
	After/cast	0.6500	<1	110	4	110	39
8 June 1999	713						
	Approval	0.6900	<1	100	6	100	29
	after/cast	0.7100	<1	110	8	110	30
13 July 1999	835						
	Approval	0.7200	<1	74	4	110	35
	After/cast	0.7200	<1	74	5	100	35
2 August 1999	906						
	Approval	0.8900	<1	74	4	110	34
	After/cast	0.9200	<1	75	5	110	34
13 August 1999	938						
	Approval	0.6800	<1	36	8	100	43
	After/cast	0.6700	<1	35	6	100	44
2 September 1999	027						
	Approval	0.7600	<1	61	4	100	35
	After/cast	0.7600	<1	63	5	100	36
15 September 1999	053						
	Approval	0.8330	<1	90	4	100	35
	After/cast	0.7900	<1	90	4	98	34
22 September 1999	075						
	Approval	0.7800	<1	51	7	11	41
	After/cast	0.7700	<1	51	8	110	41
29 September 1999	099						
	Approval	0.7200	<1	48	4	110	41
	After/cast	0.7000	<1	49	4	110	42
5 October 1999	119						
	Approval	0.6700	<1	44	7	100	35
	After/cast	0.6300	<1	44	4	100	35
5 October 1999	120						
	Approval	0.7800	<1	61	4	100	41
	After/cast	0.7800	<1	63	4	100	40
30 October 1999	215						
	Approval	0.7100	<1	78	4	100	43
	After/cast	0.6700	<1	70	4	110	42
31 October 1999	221						
	Approval	0.7000	<1	91	4	100	43
	After/cast	0.6800	<1	90	5	100	42
23 November 1999	302						
	Approval	0.7000	<1	50	5	110	37
	After/cast	0.6800	<1	54	6	110	38
28 November 1999	320						
	Approval	0.7800	<1	26	5	110	37
	After/cast	0.7200	<1	26	5	110	37
7 January 2000	479						
	Approval	0.7100	2	26	3	120	29
	After/cast	0.7400	1	26	8	120	29
31 January 2000	585						
	Approval	0.8400	2	46	3	92	33
	After/cast	0.8600	2	47	7	93	36

Table 3 (*Continued*)

Date	Lot no.	Sb (%)	Sn (ppm)	Cu (ppm)	As (ppm)	Bi (ppm)	Ag (ppm)
9 February 2000	618						
	Approval	0.6500	1	59	17	91	31
	After/cast	0.6800	1	60	18	91	31
9 February 2000	621						
	Approval	0.7000	<1	40	16	89	34
	After/cast	0.7600	1	46	11	89	34
19 February 2000	567						
	Approval	0.7100	<1	37	5	92	36
	After/cast	0.7100	1	37	4	91	33
21 February 2000	668						
	Approval	0.8250	8	61	1	92	38
	After/cast	0.7940	1	62	5	94	38
19 March 2000	774						
	Approval	0.7300	<1	58	1	92	36
	After/cast	0.6200	5	6	5	93	38
8 April 2000	847						
	Approval	0.8200	<1	40	3	99	38
	After/cast	0.7800	<1	41	8	100	39
15 April 2000	878						
	Approval	0.7200	<1	46	2	94	40
	After/cast	0.7400	<1	47	<1	94	40
24 April 2000	914						
	Approval	0.6600	<1	70	<1	89	38
	After/cast	0.6500	<1	70	<1	89	38
26 April 2000	921						
	Approval	0.8200	<1	40	<1	88	37
	After/cast	0.8000	<1	40	<1	88	37
28 April 2000	928						
	Approval	0.7720	<1	43	<1	87	37
	After/cast	0.7660	<1	44	3	87	36
10 May 2000	966						
	Approval	0.9200	<1	30	<1	90	41
	After/cast	0.9200	<1	30	1	92	40
8 May 2000	961						
	Approval	0.7300	<1	70	5	89	40
	After/cast	0.7200	<1	70	5	89	40
27 May 2000	030						
	Approval	0.8700	7	50	<1	89	38
	After/cast	0.8520	<1	51	2	92	38

the bullets from the same lot, can and do have naturally occurring and distinguishable variability in compositions.

To demonstrate our position that is based on known, real-world metallurgical casting phenomena, we considered lead alloy data used in the manufacture of 0.22 caliber LR bullets for the years 1987–1988 and 1998–2000, for one of the major ammunition manufacturers, and for the years 1998–2000 for a second major manufacturer.

For comparisons of the data, we suggest the assumption that the ICP–OES and SS–OES methods used by forensic examiners and the lead refiners have a 5–10% R.S.D. for precision, a routinely accepted value in the field of analytical chemistry. This assumption is not necessary for a valid comparison of the data but is mentioned as a general guideline. Furthermore, when an element is present at less than 10 ppm, this R.S.D. value becomes somewhat larger because of the difficulty in making an accurate measurement as the detection limits for a given element are approached. The error in absolute accuracy of ICP–OES and SS–OES can be larger or smaller, and depends on the standards used,

Table 4
Lot composition for 0.22 caliber alloy no. 2 (1987–1988)

Date	Lot no.	Sb (%)	Sn (ppm)	Cu (ppm)	As (ppm)	Bi (ppm)	Ag (ppm)
27 August 1987	094						
	Approval	0.67	<1	27	06	<1	03
	After/cast	0.66	01	30	05	88	19
24 September 1987	186						
	Approval	0.66	01	66	06	110	18
	After/cast	0.65	02	70	06	110	18
8 October 1987	238						
	Approval	0.73	02	20	07	88	16
	After/cast	0.69	01	20	07	85	17
3 November 1987	011						
	Approval	0.71	<5	100	06	84	19
	After/cast	0.77	<5	100	08	87	18
5 November 1987	018						
	Approval	0.85	06	460	08	88	12
	After/cast	0.87	05	210	08	90	16
1 December 1987	106						
	Approval	0.78	<5	21	04	87	17
	After/cast	0.77	<5	38	15	89	15
2 December 1987	112						
	Approval	0.82	<5	11	05	91	16
	After/cast	0.79	<5	12	07	89	16
11 January 1988	218						
	Approval	0.77	<5	40	07	87	17
	After/cast	0.77	<5	22	05	93	18
18 January 1988	236						
	Approval	0.70	<5	15	04	89	15
	After/cast	0.67	<5	17	05	88	16
25 January 1988	258						
	Approval	0.75	<5	34	06	90	16
	After/cast	0.65	<5	15	06	87	17
26 January 1988	262						
	Approval	0.74	<5	30	05	89	16
	After/cast	0.67	<5	40	10	89	16
3 February 1988	192						
	Approval	0.73	<5	10	05	89	15
	After/cast	0.69	<5	10	05	90	15
23 February 1988	027						
	Approval	0.72	<5	20	07	89	15
	After/cast	0.71	<5	25	06	89	15
15 March 1988	091						
	Approval	0.73	<5	16	07	90	14
	After/cast	0.67	<1	16	06	90	14
28 March 1988	130						
	Approval	0.80	<5	32	08	94	18
	After/cast	0.79	<5	33	06	92	16
30 March 1988	132						
	Approval	0.70	<5	16	05	83	16
	After/cast	0.68	<5	17	05	86	14

Table 4 (*Continued*)

Date	Lot no.	Sb (%)	Sn (ppm)	Cu (ppm)	As (ppm)	Bi (ppm)	Ag (ppm)
11 April 1988	172						
	Approval	0.78	<1	60	06	88	17
	After/cast	0.69	<1	20	05	90	16
20 April 1988	207						
	Approval	0.68	<5	37	09	88	13
	After/cast	0.75	<5	40	07	86	15
2 May 1988	235						
	Approval	0.83	<5	17	07	86	16
	After/cast	0.79	<5	20	07	89	15
2 May 1988	238						
	Approval	0.78	<5	46	07	90	15
	After/cast	0.77	<5	48	07	90	15
3 May 1988	240						
	Approval	0.71	<5	11	07	87	14
	After/cast	0.66	<5	13	06	88	15
31 May 1988	316						
	Approval	0.69	02	40	05	85	17
	After/cast	0.72	<5	23	06	89	16
9 June 1988	033						
	Approval	0.68	<5	16	06	85	15
	After/cast	0.66	<5	18	06	86	15
13 June 1988	042						
	Approval	0.77	<5	11	07	92	17
	After/cast	0.71	<5	10	05	90	17
17 June 1988	064						
	Approval	0.71	<5	22	07	88	16
	After/cast	0.69	<5	270	07	88	16
21 June 1988	070						
	Approval	0.77	<5	40	07	92	17
	After/cast	0.71	<5	41	06	90	15
28 July 1988	160						
	Approval	0.80	<5	40	10	87	14
	After/cast	0.77	<5	29	08	87	16
8 August 1988	189						
	Approval	0.75	<5	18	07	89	16
	After/cast	0.75	<5	19	08	88	14
28 August 1988	257						
	Approval	0.75	<5	24	05	86	17
	After/cast	0.75	<5	29	06	86	16
28 September 1988	043						
	Approval	0.74	<1	19	02	86	13
	After/cast	0.72	<1	40	02	86	13
29 October 1988	149						
	Approval	0.69	<1	09	08	87	15
	After/cast	0.65	<1	12	07	87	15

elemental interference, etc. The detection limits of ICP–MS [9] are generally better than the other two techniques, but the use of it requires an additional step(s) to precipitate the lead from the sample aliquot to be analyzed. One of us (WAD) has experience with this precipitation technique and we are aware of the care that must be taken when using it for lead analysis. A discussion of analytical errors and the benefits of one analytical technique over another is beyond the scope of

this paper, but is relatively unimportant to our arguments since the same technique is used to compare both questioned and known samples, and since it is the application and interpretation of the results which are germane to our concerns about "same lot" and/or made at the "same time" conclusion error rates, not the specific analytical technique per se.

Lot inhomogeneity can be most easily demonstrated by examining the data in Tables 1 and 2. Table 1 lists the composition (for the same elements) as measured at the beginning, middle, and end of the casting of each lot. Table 2 lists the average composition of each lot from one refiner for the elements antimony, tin, copper, arsenic, bismuth, and silver. The data listed in Table 1 were used to generate the data listed in Table 2. Some lots exhibit a homogeneous composition from beginning to end of the casting. For other lots, such as lots 423 and 464, there is a real and measurable variation in the alloy composition within each lot. For example, lot 423 shows a range in antimony content from 0.673 to 0.680%, a range in tin from 74 to 106 ppm, a range in copper from 207 to 247 ppm. Arsenic, bismuth and silver show essentially no variation during the casting of this lot of material. A larger compositional difference may be inferred if one adds any experimental error to these bounding values. Tables 3 and 4 list data from the second supplier where compositional data are taken for each lot at the beginning and end of each casting; they show similar variability to that from the first supplier. A comparison of the data in Tables 3 and 4, taken about 10 years apart shows that variability in composition of individual lots is a general phenomenon and not restricted to one time period only. These data confirm that each lot of lead is not necessarily compositionally homogeneous. The various compositions within each lot, with appropriate sampling methods and replication, can easily be differentiated by ICP–OES or SS–OES.

The issue of whether each lot is compositionally unique as determined by ICP–OES or SS–OES can now be addressed. With reference to Tables 1 and 2, it would be extremely difficult, if not impossible with present analytical techniques, to distinguish bullets from lots 464 and 465. Other lots of this alloy are very similar in composition and could be distinguished only by small differences in one element. In Table 3, the "analytically indistinguishable" matches are even more frequent. It is not realistic to expect to be able to distinguish among bullets from lots 589, 866 and 867, or from 750 and 192. Table 4 shows the same trends for a time period about 12 years earlier. Consider for example the compositions of the following lots: 238,258 and 240; 236, 240 and 149; 258 and 316; and finally 207 and 070. We note that these data are for a 1–2 year period only. It is reasonable to assume that there are, or could be, significantly more lots of similar compositions, given the narrow ranges of analyte presence and the total number of years of combined bullet lead alloy production.

It is important for the forensic examiner to understand that it is the intention of the lead refiner to supply the same material, lot-to-lot, per specifications, to the bullet manufacturer. There is always some variability internally in each lot and some variability lot-to-lot. However, as we have just demonstrated, there is sufficient variability within each lot's composition, and sufficient overlap in lot-to-lot compositions, to disallow, in general, the conclusion that any given bullets or groups of bullets were manufactured on or about the same day or from the same batch or lot of lead. It is incumbent on the forensic examiner to consider the variability in compositions of production ingots when interpreting the ICP–OES data found in the EAC method. Moreover, each of these variabilities is itself variable, that is, one lot may vary in composition to a greater or lesser degree for the same nominal composition than another lot from the same supplier. Any particular lot composition may, in fact, be unique, or it may be indistinguishable from one or more other lots produced that year or in previous years. The forensic examiner would have no way of knowing which is the actual case.

The ammunition manufacturer may add slightly to the variability of bullet compositions in several ways. First, both the composition and compositional variability can change in any remelting of the lead alloy pigs to produce extrusion bullets. The metallurgical phenomena of stratification and segregation can occur here as well as at the lead smelter; however, this does not alter or affect our conclusions. As the data show, each element used in the analysis is restricted to a narrow band of numerical values, that is, each has a limited numerical range. Any remelting, even if done in smaller batches, merely adds more data points within the same limited range of compositions.

The process of extrusion itself may add variability to the product. The lead cable sheathing industry has documented variability in lead cable sheathing, used for protecting underground electrical cables, that is produced in much the same way as lead wire for bullets. In the process of sheathing cable, the wires to be sheathed are fed into the extruder and a seamless lead alloy sheath is formed directly around the wire bundle in a continuous fashion. Since this is done for corrosion protection of buried cables, any non-homogeneity in sheath composition is important. Researchers have found both axial and radial variations in composition large enough to cause performance concerns. It is as yet unclear as to whether this variability is caused by the extrusion process itself or some aspect of the extruder feeding process, or is present in the feed material presented to the extruder [26,27].

Another major consideration for the forensic examiner is that bullets produced from one lot of lead may be intermingled with bullets made from a previous lot or lots of lead at the ammunition manufacturer. All of the lead pigs or billets from one lot are not necessarily consumed in one wire drawing campaign; lead from one source may go into several wire drawing campaigns. Fully formed bullets may be stored for some time before being assembled in cartridges. Previous investigators have found several, to as many as fifteen, compositional groups in the same box of ammunition. They

have also found "outliers" and variability among bullet compositions in the same box that were too large to explain using the interpretation that each bullet in a box of ammunition came from the same source of lead. The date code on the box of ammunition is only the date that the fully assembled cartridges were packaged into that box. It does not necessarily have any relationship to the date of manufacture of the bullets found in that box. We submit that these observations of multiple compositions and "outliers" within a box made by forensic examiners can be due to the common occurrence of intermixing pigs, and the intermixing of bullets from different lead alloy lots at the bullet manufacturer, as well as to same-lot variability we have demonstrated. The forensic examiner cannot readily discern which activity or phenomena is/are attributable to the composition variations.

The authors have additional concern regarding the elements chosen for measurement by the forensic community. As we have pointed out, the elements chosen for quantification in the EAC method (including Te and Cd, although we do not list these elements in the data because we only have partial data for these elements and intend to acquire it) are intentionally controlled in the refining process and hence have limited allowable ranges of compositions. They are not random minor or trace elements. Antimony is the major (and frequently the only) specified alloying element; its value is fixed within a limited range as specified by the ammunition manufacturer. The elements tin, arsenic, copper, bismuth, and silver are intentionally removed to below certain specified levels. This limits their compositional ranges. As previous researchers have found, bismuth and silver are not very discriminatory [7,8]. There is a logical and expected reason for this. Bismuth and silver, being primarily controlled by the needs of lead-acid battery manufacturers and the lead being recycled at the time, tend not to change for ammunition lead alloy production over long time periods. The secondary lead smelters do not adjust it. Note the amounts of bismuth and silver in Tables 1 and 3. Except for one lot, bismuth values are nominally 100 ppm, and silver values are nominally 25–35 ppm. The data in Table 4 for the time period 12 years earlier have bismuth values of nominally 90 ppm and silver values of nominally 17 ppm. As Keto observed, [9] there really is no reason that these elements are used in the analyses other than that they can be measured. We suggest that more meaningful and non-correlated elements be chosen if a useful method is to be developed.

It is clear that the variability and lack of uniqueness easily explain all of the "exceptions" to the method noted by several previous investigators [6,10,15]. It has been argued by some advocates of the current forensic practice of bullet lead comparisons that the analytical techniques used by the bullet lead industry are not as sophisticated, precise or accurate as those used by the forensic community. However, we feel that this is not the case. We note that the data supplied for this study by the secondary lead refiners were acquired with SS–OES or ICP–AOES, the same technique(s) used in the forensic community for many years, and that appropriate standards and calibration were used in the collection of our data.

6. Summary and conclusions

Several implicit assumptions or premises are evident from court testimonies and published articles attempting to associate bullets or bullet fragments with a "common source of lead" or the "same box of bullets". The first and very necessary assumption is that a bullet or bullet fragment is a representative sample of the molten source of lead from which it originated. The second assumption, intimately related to the first, is that the parent "source of lead" has the same, invariant composition throughout the entire "source". The third assumption is that no two melts or lots are ever produced with such similar compositions as to render them analytically indistinguishable.

The forensic opinion that a bullet(s) or bullet fragment(s) "came from the same source of lead" absolutely and unequivocally requires that all three premises be true. If any one is demonstrated to be false, the scientific validity and foundation for such a conclusion of a common source fail.

Metallurgical phenomena known to occur in refining and casting practices suggest that the forensic examiner should be cautioned that samples such as bullet fragments, or even entire bullets, may not be representative samples of their parent molten sources of lead due to compositional variability within each source. Compositional data from 1998–2000 and 1987–1988, from secondary lead refiners who supplied bullet lead used for the manufacture of bullets, as presented herein demonstrate this. The variations in composition within each "source" exhibited by the data confirm predicted and well-understood metallurgical phenomena in the refining and casting processes. These data should clearly dispel any belief that the sources of molten lead used for the manufacture of bullets are always homogeneous.

In just the 2-year period of production by only two producers of bullet lead alloys, multiple examples of "analytically indistinguishable" sources are demonstrated. When then considering the total production over a span of 20 or more years of the universe of all bullet lead suppliers, the total tonnage of possible "analytically indistinguishable" sources (overlaps) can only become larger.

Although not the subject of this particular paper, the research suggests that positive associations by reason of a "common source" by the EAC method, founded on the premises of homogeneity and uniqueness, should not survive the Daubert [28] tests and scrutiny as to empirical testing, peer review and publication, error rate, general acceptance, sufficiency of facts and data, reliability of principles/methods, reliable application of principles/methods, unjustifiable extrapolation, obvious alternatives and explanations, and

field of expertise, for an opinion rendered as to "same source of lead" or "same box of ammunition".

Based on the inhomogeneities observed in lead "sources," and of numerous demonstrated instances of multiple sources that are analytically indistinguishable, it is our conclusion that the most positive opinion that can be rendered from data that show that two or more bullets or fragments are analytically indistinguishable is that they "could have," or that "it is possible" that they had, a common source. Our literature review and research suggest that no valid statistical probability or likelihood can be attached to a conclusion of "same source of molten lead" or "same box of ammunition," even if pressed by the proponent of the evidence or the court.

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