Portable X-Ray Fluorescence of Lead Ammunition from Kettle Creek Revolutionary War Battlefield, Wilkes County, Georgia

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I. Introduction

Small arms ammunition in America, throughout the eighteenth and early nineteenth centuries, consisted of round soft-metal balls. These were mostly lead, although archeologists have documented other metals as additives. Available small arms and related ammunition varied by military unit, and included pistols, rifles, trade guns, carbines, fowlers, and large caliber wall guns, as well as American, French and English muskets. Macroscopic identification of associated bullets alone limits battlefield interpretations. Traditional analysis documents diameter, weight, firing condition (impact evidence, rifling, worming, ramrod impact, casting evidence), alterations (chewing, cutting, carving), other post-depositional damage (rodent gnawing), and archaeological context. This monograph documents a portable X-Ray fluoresence study by the LAMAR Institute of lead ammunition from the Kettle Creek Revolutionary War battlefield in Wilkes County, Georgia. This study builds on the recent research by the author and others on elemental analysis using pXRF on eighteenth- and early nineteenth-century military sites in the eastern United States (Seibert et al. 2014; Elliott 2016; Elliott and Seibert 2017).

History of Lead Mining

Lead mining in North America in the colonial and Revolutionary War era was widespread quite limited in scope. The American patriots were at a considerable disadvantage against the British in their access to lead for ammunition. Lead was mined in Connecticut, Massachusetts, New York, Pennsylvania and Virginia (Ingalls 1908:87-88; Marteka 2009; Ingalls 1907:980; 1908:88; Van Tassel 2017; Sims and Hotz 1951:107; FortRoberdeau.org 2014; Columbian Magazine 1788:703; Stapleton 1971:361-371; Whisonant 1996; 2015; Wood 2014; Avocamuseum.org 2014; McGavock Papers 1760-1788; Austin 1977). Lead deposits were discovered and mined in Kentucky and West Virginia soon after the American Revolution (Filson 2009:20; Imlay 2013:21, 53)

Lead was mined in French Louisiana, present-day southeast Missouri, as early as 1721. Early mining operations also were established at Mine La Motte. Lead ore was taken from the mines down the Mississippi River to Saint Genevieve and eventually to France (Seeger 2008:5, 10). The lead mining operations at Mine La Motte ceased in 1769, when it was destroyed by Chickasaw Indians. Mining there did not resume until 1780 or 1782 (Ingalls 1907:981). Filson (2013:21) noted in 1793, “the lead mine on the Mississippi must prove inexhaustible. It extends from the mouth of Rock river more than 100 miles upwards. Besides these there are several others, some of which lie on the Spanish side of the Mississippi, and have been used for years past.” No records have been found to indicate that the Old Lead Belt deposits in Missouri contributed significantly to the ammunition used in the American Revolution, although little or no primary research has been done on the topic.

To date we have located no documentary evidence for any Revolutionary War era (or earlier) lead mines in the Carolinas and Georgia. The lack of documentation does not mean that no lead was mined in those three states, as all three states possess lead deposits. The lack of any reference to lead mines or lead mining in the southern colonies suggests that, if any took place, it was on a local scale and failed to catch the notice of state politicians or military leaders.

Lead mines or lead prospects are known from the nineteenth and twentieth centuries in Georgia . These include: Rich mine and Evalee Richards prospect, Cherokee County; Magruder mine and Seminole/Magruder/Wardlaw/Jackson veins, Lincoln County; Landers, Tatham and Woodall mines, McDuffie County; Earnest Galena prospect, Murray County; Mcgarrity Prospect, Paulding County; Shiloh Church prospect, Polk County; McKenzie Mine, Quitman County; Habersham County occurrences; Rabun County; H. Amason prospect, Troup County; and the Chambers mine, Wilkes County.

South Carolina also had lead mines in the nineteenth and twentieth centuries. These include: An unnamed barite mine, Cameron, Kings Creek, Lavender Place, Silver Mine Ridge, The Big Incline, Wallace Gold Mine and West Hill mines and Northeast Barite Pit and Kings Creek Barite Southwest Area, Cherokee County; Barite Hill mine, McCormick County; and Wright mines and Castles and McKnight prospects, York County.

North Carolina also later lead mines by the nineteenth and twentieth centuries. These include: Lead mine, Alexander County; Morganton, Burke County; Rocky River mine, Cabarrus County; and Silver Hill, Davidson County (1838).

Great Britain abounds in major lead deposits, which have been mined since at least Roman times. England was a major producer of lead (Percival 1774:33, 36; Pilkington 2007:95-130; Pryce 2010:243). Lead also was mined in Ireland since at least 1667 (Petty 2007:vi).

II. Methods

Portable X-Ray Fluorescence Analysis in Archaeology

Previous study of eighteenth- and early nineteenth-century lead artifacts from archaeological sites provide a backdrop for the present study (Sivilich 1996, 2004, 2014; Branstner 2008). These studies explored various physical aspects and characteristics of round ball ammunition.

Portable X-Ray Fluorescence (pXRF) has been used for several decades as a non-destructive method of analyzing archaeological artifacts and sediments. Hunt and Speakman (2014) point out many of the problems and pitfalls in pXRF studies of archaeological materials.

A recent study by Siebert and colleagues from National Park Service, Southeast Archeological Center and Bruce Kaiser examined lead shot from Palo Alto battlefield, Mexican-American War, 1846 (Seibert et al. 2016). Their study analyzed 700 lead shot. They were able to distinguish between shot from Mexican (British Brown Bess, Indian Pattern) weapons and shot from American (Springfield Arsenal, Model 1816/1822 and 1835 muskets). The simplified result is that Mexican shot contained more silver (Ag).

In his recent book on musket balls, Daniel Sivilich (2016) presented some information on pXRF results from six musket balls from Valley Forge, Pennsylvania and 104 musket balls from Monmouth Battlefield in New Jersey. He compare the frequencies of lead, iron and tin in these balls.

In 2015 archaeologists Michael Seibert and Dan Elliott conceived a pilot study using pXRF technology to identify and characterize round ball ammunition from early sites (primarily Revolutionary War period) in the eastern states. They were joined in this endeavor by archaeologist Meg Waters, who had recently recovered a small sample from the Parker's Revenge battlefield in Massachusetts. On the advice of Bruce Kaiser, inventor of the Bruker Tracer handheld device, the archeologists attempted to gather data systematically. Data files for the study were collected by Siebert and Elliott with Bruker Tracer III devices. Data was collected for 180 seconds for each sample using 45 kV voltage and 20 µA and Bruker's Green filter (Ti/Al). No vacuum was employed. On December 4 and 5, 2015 a meeting of the National Park Service and the LAMAR Institute archaeologists was held at NPS Southeastern Archeological Center in Tallahassee, Florida. This study demonstrated that Portable X-ray Florescence (pXRF) is a useful technology in distinguishing round ball assemblages from eighteenth and early nineteenth century sites in the eastern United States. This pilot study gathered elemental data on 440 round metal balls through a systematic data collection protocol. This sample was obtained from 14 different archeological sites from the U.S. Eastern seaboard with emphasis on the southeast. The sample spans the early eighteenth century through early nineteenth centuries and it covers Native American and Euro-American towns, as well as French and Indian War, Revolutionary War, Indian Wars, and War of 1812 sites.

These data demonstrated that Antimony (Sb) and Tin (Sn) are very important elements for measuring differences in round balls. These two elements are common components of pewter. Bullet elemental composition varies over time and space from 1720s to 1820s.

The preliminary findings from the pilot study demonstrated that Portable X-ray Florescence (pXRF) can be a useful technology in distinguishing round ball assemblages from eighteenth and early nineteenth century sites in the eastern United States. Bruce Kaiser confounded the group by announcing a new and improved filter for the Bruker Tracer, which he called the “Black Filter”. This filter had the additional of thin copper sheets and was designed to reduce the masking effect caused by lead in the round balls. The group then proceeded to sample 72 lead balls from a variety of sites using the Black filter. The task before us is to solidify the pXRF data collection protocol so that an international database can be created and maintained. The group agreed that the database should be housed and maintained by the National Park Service. We also agreed that the breadth of the database should be widened to include the international community.

Currently we are lacking elemental data on eighteenth and early nineteenth century lead sources. A pXRF study of those lead sources will further strengthen the value of this database in understanding those relatively anonymous round bullets that are the building blocks of conflict studies. Collecting lead samples from early mines in both America, Great Britain and Europe is a high priority task.

Archeologists can improve on the lead ball information by incorporating pXRF analysis of the lead balls into existing analytical framework. The ultimate goal is to elevate the diagnostic value of round ball ammunition so that we can determine where the lead came from, who was firing the bullets, and how did access to lead vary over the course of history. This now appears to be an achievable goal (Elliott and Seibert 2017). Researchers are encouraged to provide input in improving this database.

Archeologists have made significant advances in musket ball analysis and interpretation over the past several decades. Musket ball diameters, represented in calibers (hundredths of inches) generally are associated with the following arms:

- American Long Rifle- .38-.51
- Fusil, American Musket, Long Rifle, Fowling Gun- .52-.59
- French Standard- .60-.66
- British Standard- .67-.74

Buck shot ranging between .29-.35 caliber were used by the Americans in buck-and-ball loads in smoothbore muskets. These were prepared paper cartridge loads that contained one large ball and two to three buck shot. The scatter of buck shot on the battlefield provides supporting information on the American firing patterns. Some Loyalist units also used buck-and-ball loads, so its presence is not an absolute indication of Patriot’s firing. Buck shot also was used in non-military contexts for hunting.

Methods Employed in the Kettle Creek Elemental Analysis

The Kettle Creek ammunition analysis was funded by the Kettle Creek Battlefield Association (KCBA) through a gracious donation from Dr. David Noble. Elemental data collection was conducted by Daniel T. Elliott with the assistance of David Noble on December 14, 2016 at the Washington-Wilkes Museum in Washington, Georgia. Data was collected for 62 lead round balls that were recovered from the LAMAR Institute's 2008 reconnaissance survey project at Kettle Creek battlefield and New South Associates' 2016 Phase I survey for a planned interpretive trail through the battlefield (Elliott 2008; Patch 2016). Elemental analysis also was conducted on two iron case shot and one Enfield bullet (Confederate Civil War ammunition type) that were recovered from the battlefield. Samples were collected using a Bruker III-V handheld device for 180 seconds each using the Black filter. Energy settings were 45 kV voltage, and 20 µA of current.

III. Kettle Creek Sample

It is against the previously described scientific backdrop that an elemental analysis of the lead ammunition and related items from the Kettle Creek battlefield was set. Data were collected for 62 round balls,as well as two iron case shot and one (Civil War era) Enfield bullet. Examples of these artifacts are shown in Figures 1 and 2. The sample includes one British Standard musket ball, one Charleville musket ball, nine Fusil balls and 51 American Rifle balls. The low frequency of British and Charleville balls reflects the fact that the engagement at Kettle Creek pitted Georgia and South Carolina militia against newly recruited Loyalists. The battle did not include any officers or enlisted men from the Continental Army or British Regulars, both of whom generally were armed with larger caliber weapons. The Fusil and Rifle balls likely were fired by combatants from both sides—Patriot and Loyalist. Key project data generated from Bruker's Artax software is included as a spreadsheet in Table 1.

Figures 3 through 5 show portions of the spectra for the Kettle Creek samples. Nickel (Ni), Hafnium (Hf), Copper (Cu), Zinc (Zn), Silver (Ag), Nickel (Ni), Hafnium (Hf), Copper (Cu), Zinc (Zn), Zirconium (Zr), Silver (Ag), Cadmium (Cd), Tin (Sn) and Antimony (Sb) all display peaks in these graphs. Table 1 contains a summary of key element data, ratios and cluster analysis groupings for the Kettle Creek sample.

We examined the relationship between Silver (Ag), Antimony (Sb) and Tin (Sn) in the Kettle Creek data. This was accomplished by expressing each as a ratio relatiave to the Rhodium (Rh) values, which represents a constant in the Bruker Tracer hardware.

The Silver (Ag)/Rhodium (Rh) ratios were ranked by weapon type. The results were British Standard, 2.364; Charleville, 2.815; Fusils, range from 3.494 to 125.840, average 4.434; and rifles, range from 0.914 to 12.535, average 3.277. Fusil and Rifle balls tend to have higher Silver (Ag)/Rhodium (Rh) ratios than British Standard or Charleville balls.

The Antimony (Sb)/Rhodium (Rh) ratios were ranked by weapon type. The results were British Standard, 2.485; Charleville, 8.019; Fusils, range from 0.469 to 125.840, average 23.948; and Rifles, range from 0.631 to 77.875, average 9.249. Fusil balls tend to have higher Antimony (Sb)/Rhodium (Rh) ratios than Rifle, Charleville or British Standard balls.

The Tin (Sn)/Rhodium (Rh) ratios were ranked by weapon type. The results were British Standard, 13.485; Charleville, 89.037; Fusils, range from 5.321 to 93.733, average 42.679; and Rifles, range from 3.506 to 594.350, average 43.562. The Charleville ball has a higher value than the British Standard ball or the Fusil and Rifle averages.

Cluster analysis was performed on Silver (Ag)/Rhodium (Rh), Antimony (Sb)/Rhodium (Rh) and Tin (Sn)/Rhodium (Rh) ratios in the Kettle Creek sample. Five clusters were identified (Table 2 and Figures 6 and 7). The dominant cluster (Segment 1) contained 33 of 62 total items (53.2% of the assemblage). Mean/centroids for this cluster were Antimony (Sb)/Rhodium (Rh), 5.95, Tin (Sn)/Rhodium (Rh), 24.03 and Silver (Ag)/Rhodium (Rh), 2.11.

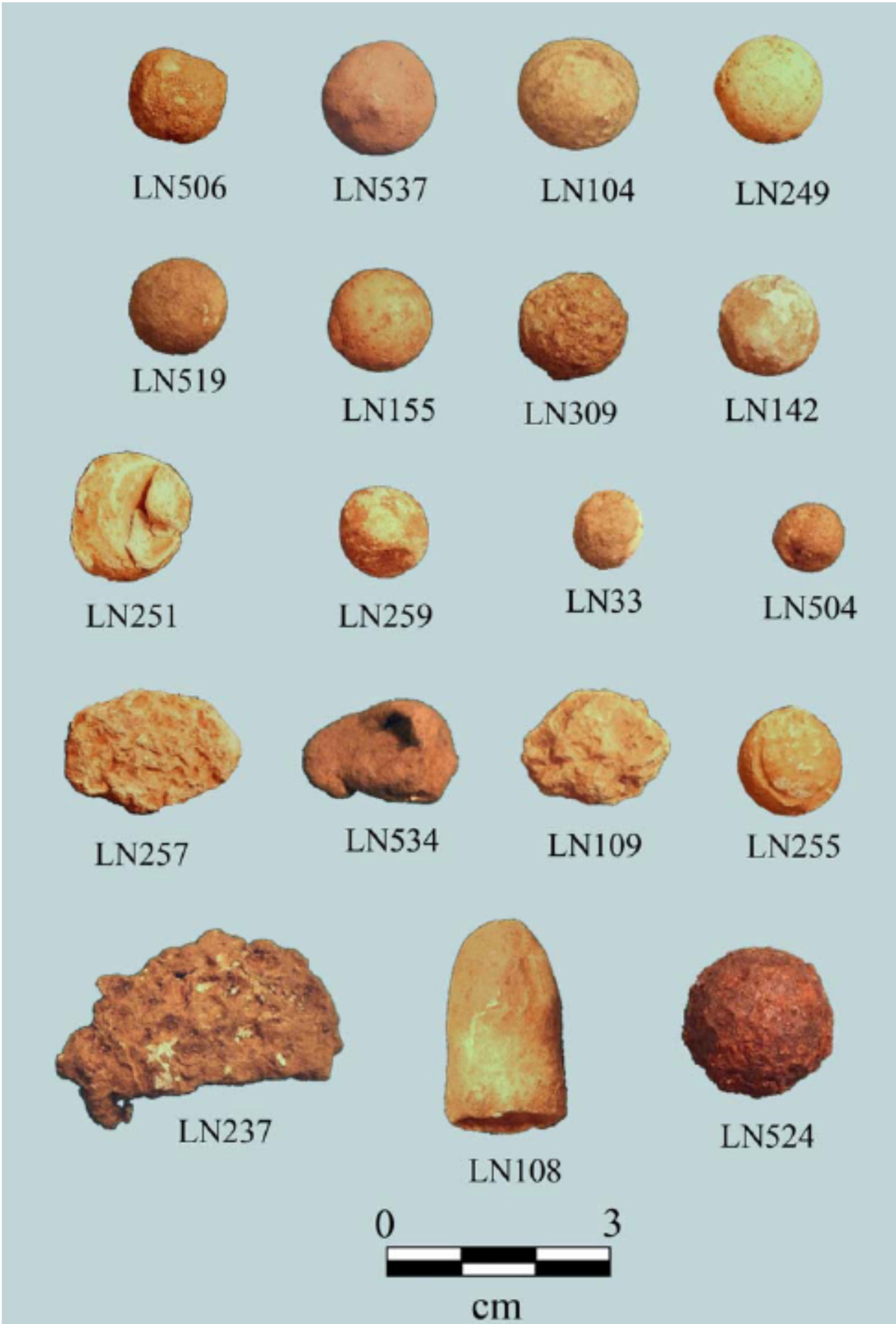

Figure 1. Examples of Ammunition Recovered by LAMAR Institute (Elliott 2008: 111, Figure 32).

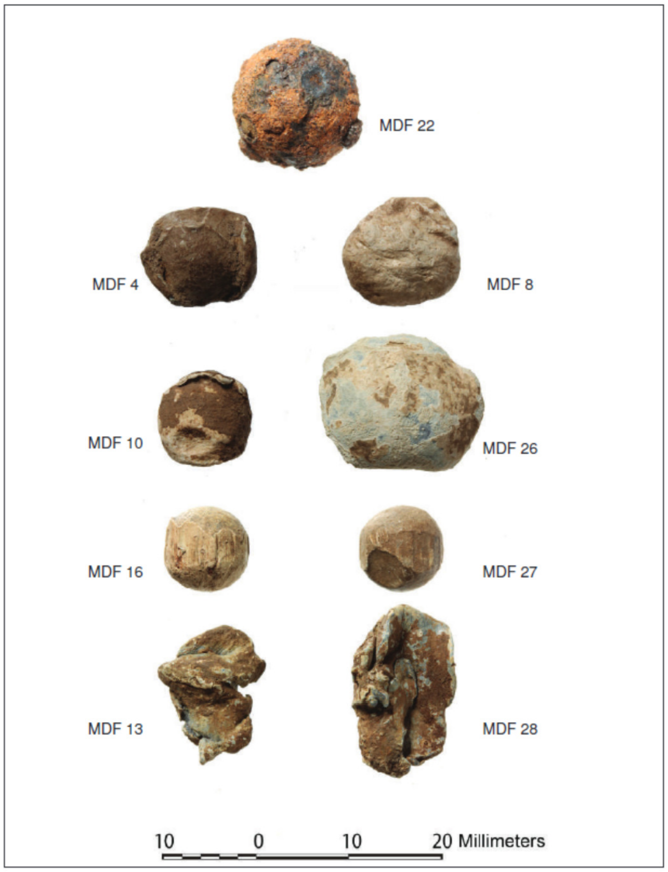

Figure 2. Round Ball Ammuntion Recovered by New South Associates (Patch 2016:23, Figure 10).

Table 1. Kettle Creek Munitions Elemental Data.

Lot No.	Diam in.	Wt. g	Weapon	Ag K12	Cd K12	Cu K12	Fe K12	Hf L1	Ni K12	Pb L1	Pb M1	Pd K12	Rh K12	Sb K12	Sn K12	Ti K12	Zn K12	Zr K12	Sb/Rh	Sn/Rh	Ag/Rh	Cluster Ratio	Cluster Count
237	0.68	28.4	British Stnd.	78	136	21	799	375	127	88226	353	44	33	82	445	86	39	556	2.485	13.485	2.364	1	2
154	0.64	17.5	Charleville	152	195	4	576	380	123	101859	579	98	54	433	4808	87	38	463	8.019	89.037	2.815	1	4
109	0.574	17.0	Fusil	94	52	8	1814	278	113	69715	278	29	33	294	3029	113	11	437	8.909	91.788	2.848	1	2
522	0.576	17.2	Fusil	185	156	27	1570	347	89	86888	160	66	56	50	298	121	59	479	0.893	5.321	3.304	1	4
250	0.60	12.3	Fusil	107	138	6	769	364	113	89516	483	88	50	217	2094	45	3	377	4.340	41.880	2.140	1	4
518	0.60	16.7	Fusil	148	112	17	1190	330	101	84944	186	78	77	269	4496	95	51	500	3.494	58.390	1.922	1	4
521	0.56	13.5	Fusil	216	119	36	848	357	122	82145	174	61	25	3146	336	116	39	492	125.840	13.440	8.640	2	1
309	0.56	13.9	Fusil	173	157	35	568	368	169	91938	416	59	30	1654	2812	69	72	508	55.133	93.733	5.767	2	1
104	0.56	15.8	Fusil	269	137	46	951	457	139	98243	230	59	72	1069	3775	77	10	599	14.847	52.431	3.736	3	1
312		14.5	Fusil	142	124	20	1612	389	95	84817	179	47	33	53	685	100	64	444	1.606	20.758	4.303	3	4
529	0.564	16.2	Fusil	355	145	116	1049	460	141	91390	235	45	49	23	312	83	77	543	0.469	6.367	7.245	5	5
45	33	3.4	Rifle	76	134	1	472	322	131	88881	460	54	77	1765	270	66	25	399	22.922	3.506	0.987	1	1
40	0.34	3.4	Rifle	97	107	1	357	219	127	84419	536	61	53	1657	198	36	27	432	31.264	3.736	1.830	1	1
44	0.32	3.4	Rifle	82	89	7	200	220	135	76338	555	42	33	1370	208	47	34	329	41.515	6.303	2.485	1	1
249	0.53	14.1	Rifle	87	196	15	598	397	147	109862	686	112	65	41	272	119	52	507	0.631	4.185	1.338	1	2
33	0.37	4.5	Rifle	102	141	26	1610	419	108	88828	176	45	55	81	251	144	31	588	1.473	4.564	1.855	1	2
155	0.54	12.8	Rifle	82	152	24	987	293	126	92265	312	82	53	72	295	106	61	485	1.358	5.566	1.547	1	2
514	0.39	3.5	Rifle	91	185	1	473	345	81	97263	500	70	50	47	293	95	19	453	0.940	5.860	1.820	1	2
247	0.48	10.0	Rifle	60	124	52	1850	378	110	79538	287	58	57	172	337	81	78	723	3.018	5.912	1.053	1	2
508	0.44	7.5	Rifle	53	136	46	1817	449	127	98696	341	44	58	47	346	74	212	579	0.810	5.966	0.914	1	2
149	0.36	4.2	Rifle	71	162	1	538	350	147	91489	396	54	46	53	275	58	32	434	1.152	5.978	1.543	1	2
MDF8	0.34	3.6	Rifle	106	164	10	538	439	148	105031	491	101	48	66	333	68	45	469	1.375	6.938	2.208	1	2
151	0.33	3.9	Rifle	79	131	19	299	322	97	86123	511	58	33	68	231	90	17	372	2.061	7.000	2.394	1	2
144	0.51	12.6	Rifle	97	108	16	745	367	106	93235	446	71	44	57	348	66	26	455	1.295	7.909	2.205	1	2
313	0.45	5.0	Rifle	49	199	30	1096	420	123	107108	388	76	38	180	344	118	18	533	4.737	9.053	1.289	1	2
248	0.54	13.0	Rifle	81	121	6	1341	279	105	89820	327	67	29	69	292	79	44	494	2.379	10.069	2.793	1	2
MDF13		3.3	Rifle	69	147	1	372	408	142	93817	519	67	25	25	257	74	33	441	1.000	10.280	2.760	1	2
MDF27	0.38	5.0	Rifle	104	130	17	568	304	170	85298	317	62	41	79	529	93	6	444	1.927	12.902	2.537	1	2
259	0.47	8.4	Rifle	87	162	40	3081	290	115	88312	188	49	54	340	854	101	-5	442	6.296	15.815	1.611	1	2
661	0.50	12.7	Rifle	79	196	30	684	393	140	103122	482	52	62	55	1893	100	26	555	0.887	30.532	1.274	1	2
532	0.374	4.7	Rifle	68	156	1	915	333	113	85159	189	52	24	244	2028	122	33	489	10.167	84.500	2.833	1	2

Table 1. Kettle Creek Munitions Elemental Data.

Lot No.	Diam in.	Wt. g	Weapon	Ag K12	Cd K12	Cu K12	Fe K12	Hf L1	Ni K12	Pb L1	Pb M1	Pd K12	Rh K12	Sb K12	Sn K12	Ti K12	Zn K12	Zr K12	Sb/Rh	Sn/Rh	Ag/Rh	Cluster Ratio	Cluster Count
38	0.444	7.9	Rifle	57	153	1	312	329	136	84880	419	54	20	177	1814	26	40	366	8.850	90.700	2.850	1	2
310	0.54	13.9	Rifle	98	133	9	548	359	157	80469	320	54	54	284	6452	81	37	384	5.259	119.481	1.815	1	2
513		13.3	Rifle	112	161	47	1452	443	63	100106	316	77	46	174	292	160	84	887	3.783	6.348	2.435	1	4
528	0.512	12.1	Rifle	106	68	19	630	347	104	74822	229	40	33	202	222	94	30	406	6.121	6.727	3.212	1	4
MDF16	0.38	5.0	Rifle	108	148	1	374	311	133	96192	516	88	82	103	552	107	17	430	1.256	6.732	1.317	1	4
142	0.52	12.3	Rifle	112	180	14	503	380	144	112893	646	104	50	232	389	33	0	544	4.640	7.780	2.240	1	4
MDF26	0.49	10.3	Rifle	109	204	14	343	445	151	105832	646	83	36	35	316	64	70	445	0.972	8.778	3.028	1	4
152	0.45	8.3	Rifle	124	204	1	595	430	139	101177	539	49	34	2265	243	65	33	490	66.618	7.147	3.647	2	1
86	0.435	7.4	Rifle	206	107	44	955	330	128	78571	289	55	24	1869	251	70	31	594	77.875	10.458	8.583	2	1
37	0.44	7.9	Rifle	258	170	27	860	413	110	94448	362	60	50	2146	3233	57	15	475	42.920	64.660	5.160	3	1
42	0.42	4.7	Rifle	86	117	8	696	329	140	89181	423	64	25	24	486	86	40	380	0.960	19.440	3.440	3	2
504	0.37	3.7	Rifle	201	171	15	823	340	118	99522	297	92	56	810	248	99	21	497	14.464	4.429	3.589	3	4
506	0.49	10.0	Rifle	245	184	44	941	446	119	98498	283	94	58	188	295	81	0	507	3.241	5.086	4.224	3	4
MDF10		3.3	Rifle	196	142	13	861	384	175	90589	289	88	55	69	299	86	51	437	1.255	5.436	3.564	3	4
110	0.52	12.3	Rifle	119	140	5	567	419	142	91850	513	59	37	382	241	119	51	404	10.324	6.514	3.216	3	4
510	0.49	10.9	Rifle	107	116	48	300	339	128	87714	575	72	33	879	287	31	30	434	26.636	8.697	3.242	3	4
537	0.53	13.4	Rifle	160	169	7	1097	364	137	96629	153	63	37	91	327	162	59	659	2.459	8.838	4.324	3	4
539	0.41	6.9	Rifle	169	163	1	2635	358	103	86913	296	33	37	139	1274	165	54	570	3.757	34.432	4.568	3	4
MDF4	0.379	4.9	Rifle	125	158	1	1320	336	120	77278	147	55	32	194	1418	158	73	716	6.063	44.313	3.906	3	4
519	0.50	10.4	Rifle	172	135	24	894	364	80	94160	322	45	46	111	2476	51	30	484	2.413	53.826	3.739	3	4
534	0.54	14.2	Rifle	123	148	15	691	351	126	83753	247	63	32	458	1824	69	78	471	14.313	57.000	3.844	3	4
523	0.35	3.8	Rifle	175	205	25	1187	424	131	94293	263	50	47	232	4746	68	-8	462	4.936	100.979	3.723	3	4
36	0.53	13.2	Rifle	274	155	19	1593	417	106	90925	168	66	58	283	291	136	68	628	4.879	5.017	4.724	3	5
517	0.43	6.9	Rifle	149	249	36	1271	430	112	93512	295	79	63	89	16539	69	95	605	1.413	262.524	2.365	4	3
257	0.52	7.0	Rifle	117	178	26	351	363	107	83361	399	53	42	143	15148	50	74	498	3.405	360.667	2.786	4	3
254	0.34	3.8	Rifle	93	205	15	716	271	119	81527	427	43	60	206	35661	91	14	530	3.433	594.350	1.550	4	3
255	0.53	12.8	Rifle	68	163	29	683	393	105	101673	496	76	11	30	248	60	44	525	2.727	22.545	6.182	5	2
509	0.38	5.1	Rifle	114	155	7	920	395	125	87917	144	55	19	43	250	79	56	542	2.263	13.158	6.000	5	4
520	0.41	5.0	Rifle	221	142	51	622	309	118	79671	227	21	28	122	759	115	21	413	4.357	27.107	7.893	5	4
505	0.49	10.5	Rifle	331	165	1	817	378	112	102880	329	78	54	100	293	72	43	569	1.852	5.426	6.130	5	5
39	0.45	8.2	Rifle	539	142	19	1465	383	107	97354	221	55	43	45	279	110	5	609	1.047	6.488	12.535	5	5

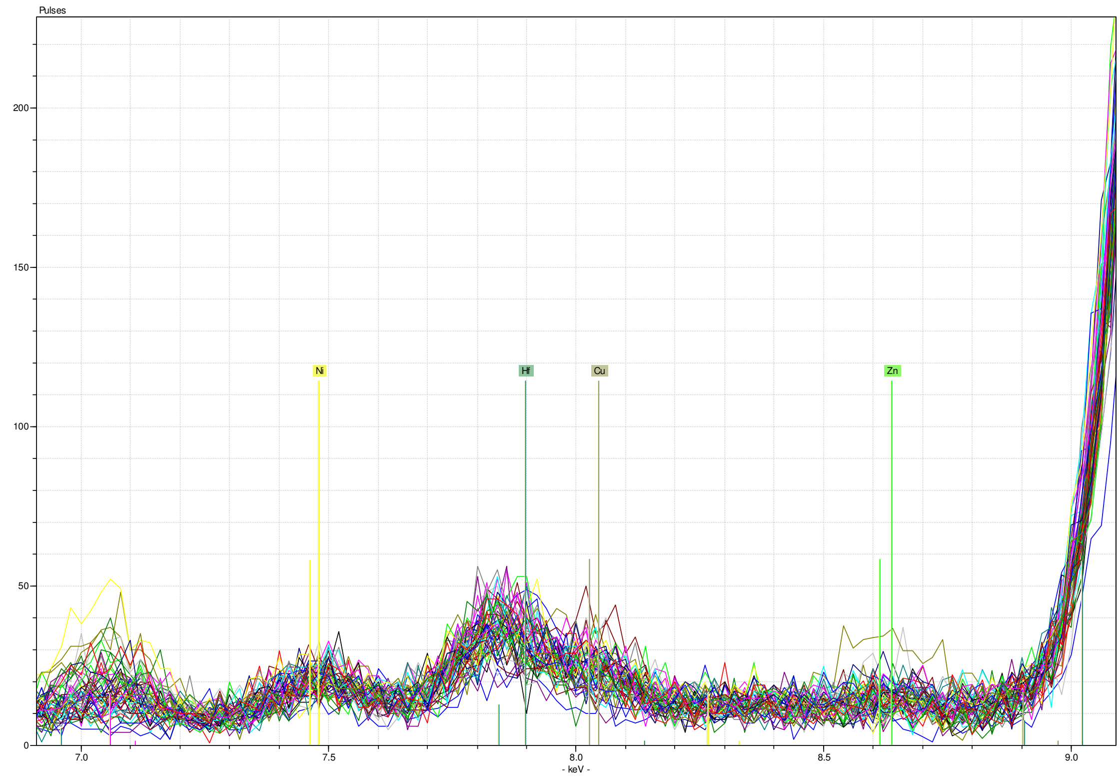

Figure 3. Spectra of Nickel (Ni), Hafnium (Hf), Copper (Cu) and Zinc (Zn), All Samples from Kettle Creek.

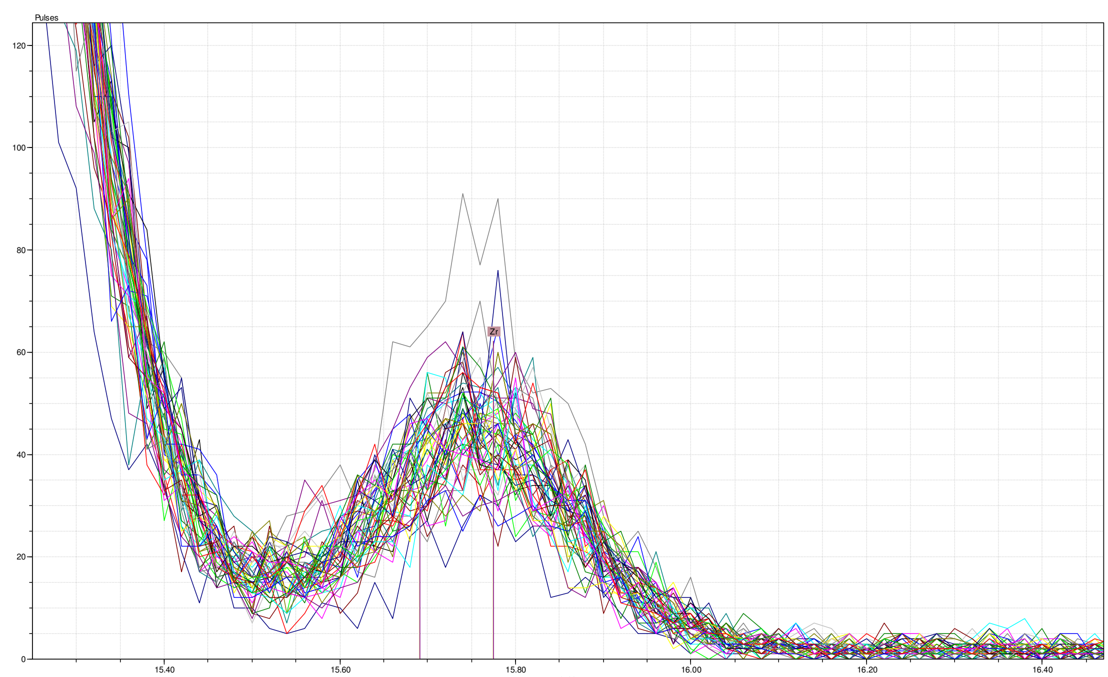

Figure 4. Spectra of Zirconium (Zr), All Samples from Kettle Creek.

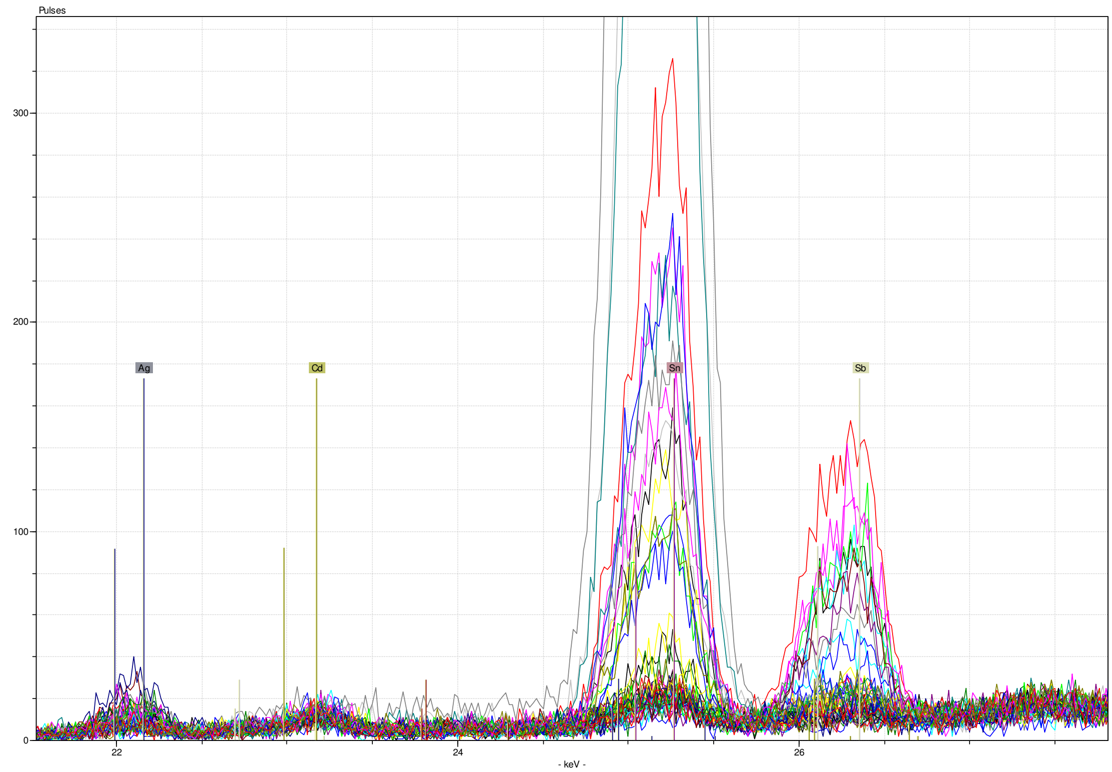

Figure 5. Spectra of Silver (Ag), Cadmium (Cd), Tin (Sn) and Antimony (Sb), All Samples from Kettle Creek.

Cluster analysis was performed on Silver (Ag)/Rhodium (Rh), Antimony (Sb)/Rhodium (Rh) and Tin (Sn)/Rhodium (Rh) ratios in the Kettle Creek sample. Five clusters were identified (Table 2 and Figures 6 and 7). The dominant cluster (Segment 1) contained 33 of 62 total items (53.2% of the assemblage). Mean/centroids for this cluster were Antimony (Sb)/Rhodium (Rh), 5.95, Tin (Sn)/Rhodium (Rh), 24.03 and Silver (Ag)/Rhodium (Rh), 2.11.

Table 2. Output for Five Clusters/Segments, Silver (Ag)/Rhodium (Rh), Antimony (Sb)/Rhodium (Rh) and Tin (Sn)/Rhodium (Rh) Ratios, Kettle Creek Sample.

Mean/Centroid	*Sb/Rh*	*Sn/Rh*	*Ag/Rh*	*0*	*0*
Segment 1	5.95	24.03	2.11		
Segment 2	81.37	31.19	6.66		
Segment 3	9.69	30.74	3.96		
Segment 4	2.75	405.85	2.23		
Segment 5	2.12	13.52	7.66		
AVERAGE	11.25	43.68	3.42		
Respondents	**Number**	**%**	**SSE/Segment**		
Segment 1	33	53.2%	37292.0		
Segment 2	4	6.5%	8147.9	**SSE Total**	**59.0**
Segment 3	16	25.8%	0.0		
Segment 4	3	4.8%	58119.7		
Segment 5	6	9.7%	472.9		
TOTAL	62	100.0%			

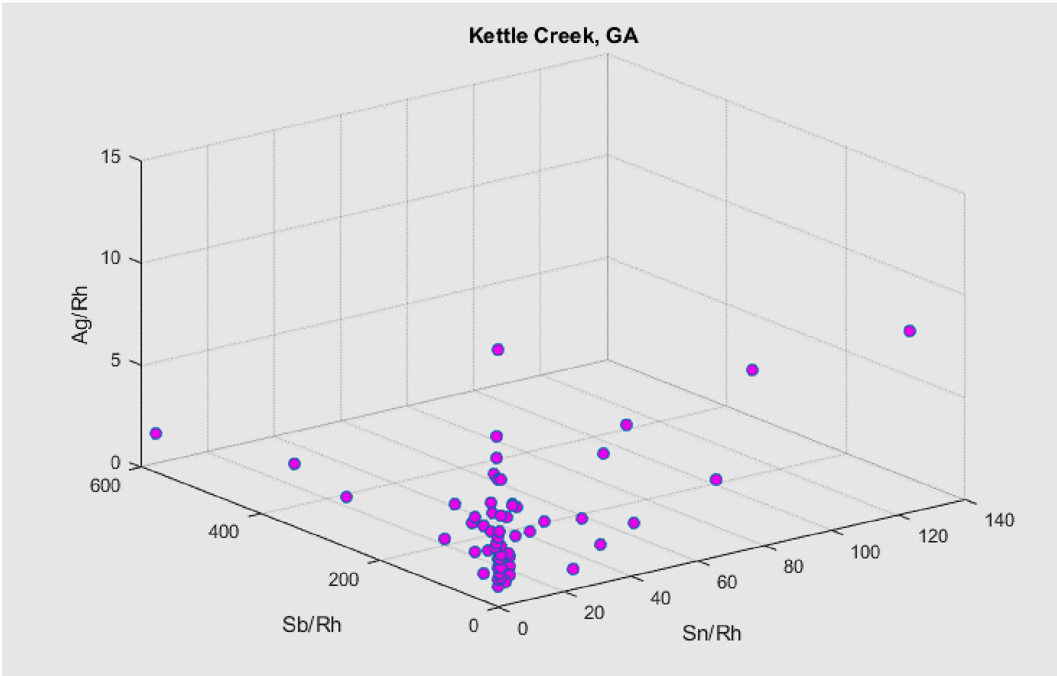

Figure 6. Scatterplot of Silver (Ag)/Rhodium (Rh), Antimony (Sb)/Rhodium (Rh) and Tin (Sn)/Rhodium (Rh) ratios, Kettle Creek Sample.

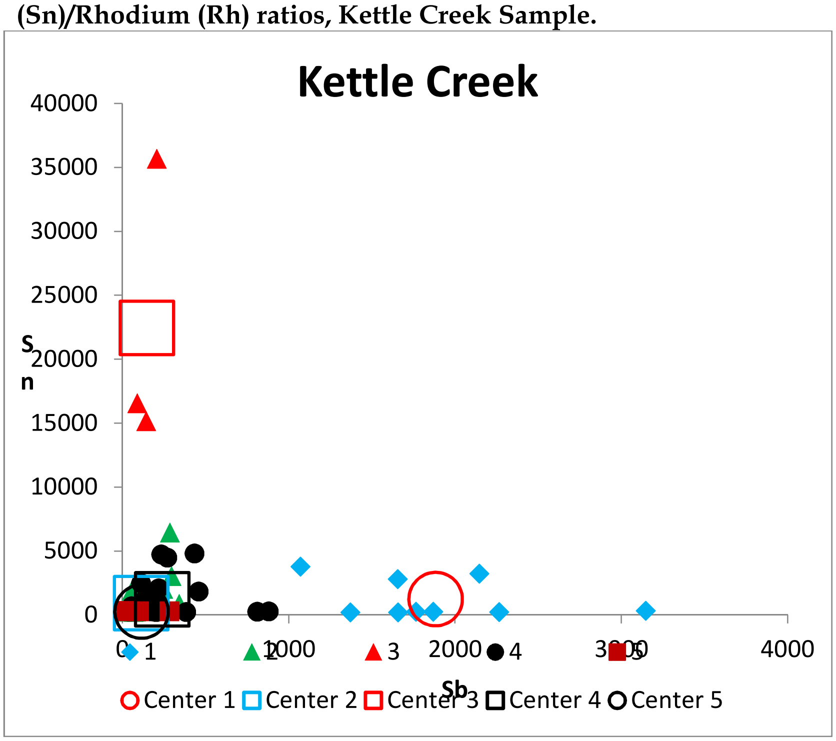

Figure 7. Central Means Chart for Five Segments, Silver (Ag)/Rhodium (Rh), Antimony (Sb)/Rhodium (Rh) and Tin (Sn)/Rhodium (Rh) Ratios, Kettle Creek Sample.

Pearson's Chi-square tests was run on these results to determine if the clusters defined for the three ratios (Silver (Ag)/Rhodium (Rh), Tin (Sn)/Rhodium (Rh) and Antimony (Sb)/Rhodium

(Rh)) were significant when compared with the results by bullet size, or Weapon Group (Rifles, Fusils, Charleville and British Standard balls) (Table 3). This exercise yielded a Chi-square value of 7.851, 12 degrees of freedom and a P value of 0.7967. The null hypothesis, which states that the frequency distribution of certain events observed in the sample is consistent with the theoretical distribution, is rejected. The alternative hypothesis, that there is a difference between the distributions, is accepted at the 0.01 confidence level. These results are consistent with previously collected elemental data from the Purysburg, South Carolina and Brier Creek, Georgia battlefields (Elliott and Seibert 2017).

The current dataset from the Kettle Creek battlefield contains information on several elements that are now recognized as important elements in the differentiation of the elemental characterization of round ball ammunition. Each of these elements is discussed.

Table 3. Chi-Square Calculations, Two-way Contingency Table, Ag, Sb and Sn Ratios by Weapon Group, Kettle Creek.

	Kettle Creek Balls					
	Cluster 1	**Cluster 2**	**Cluster 3**	**Cluster 4**	**Cluster 5**	
Rifles	27 *27.05* (0.00)	2 *3.86* (0.90)	14 *13.14* (0.06)	3 *2.32* (0.20)	5 *4.64* (0.03)	**51**
Fusils	6 *6.89* (0.12)	3 *0.98* (4.12)	3 *3.35* (0.04)	0 *0.59* (0.59)	1 *1.18* (0.03)	**13**
Charleville	1 *0.53* (0.42)	0 *0.08* (0.08)	0 *0.26* (0.26)	0 *0.05* (0.05)	0 *0.09* (0.09)	**1**
British Standard	1 *0.53* (0.42)	0 *0.08* (0.08)	0 *0.26* (0.26)	0 *0.05* (0.05)	0 *0.09* (0.09)	**1**
	35	**5**	**17**	**3**	**6**	**66**

$\chi^2 = 7.851$, df = 12, χ^2/df = 0.65, $P(\chi^2 > 7.851) = 0.7967$

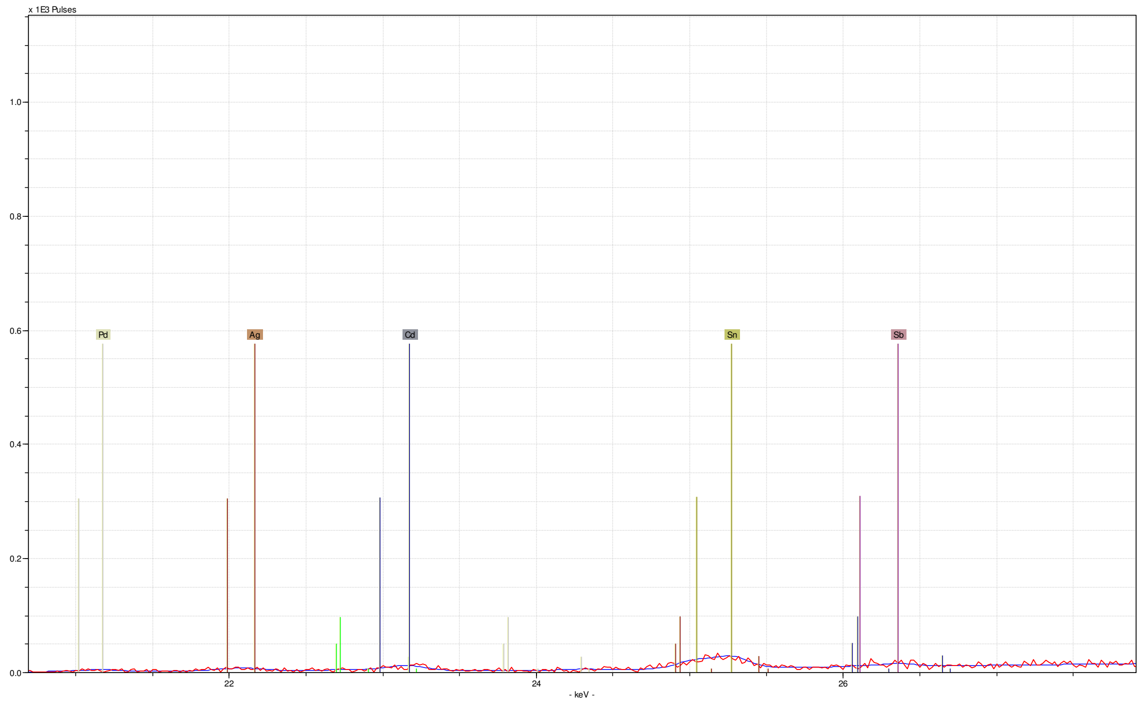

Figure 8. Spectra for British Standard Ball, showing Silver (Ag), Cadmium (Cd), Tin (Sn) and Antimony (Sb).

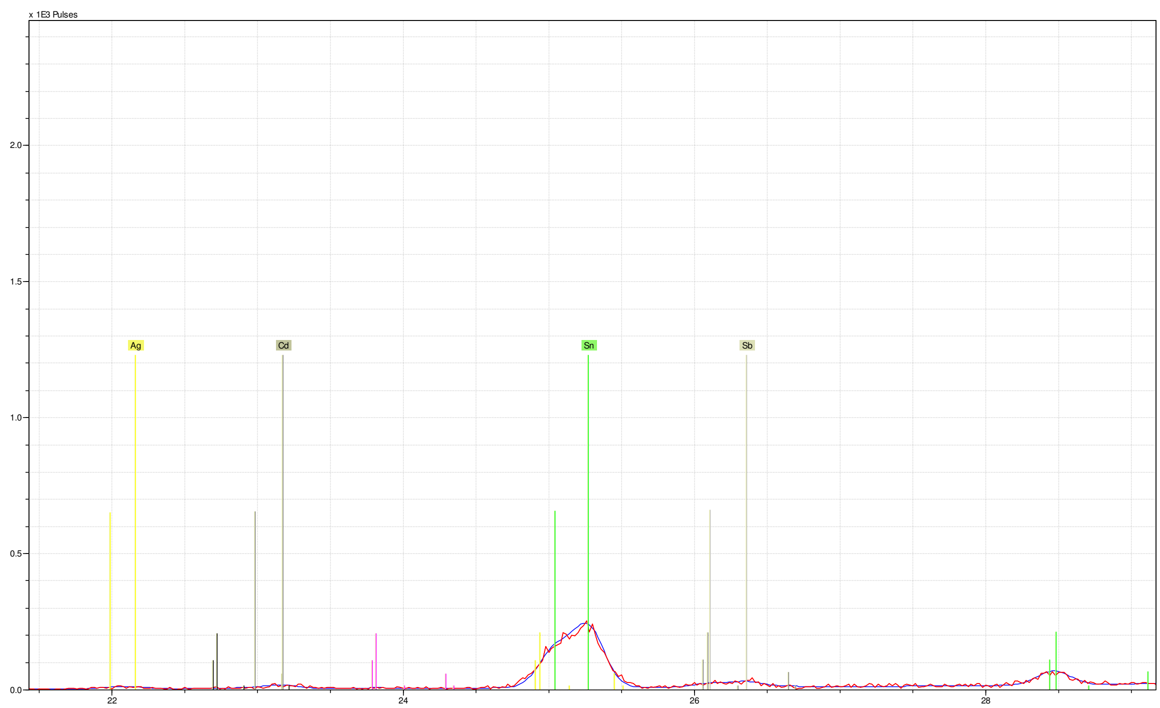

Figure 9. Spectra for Charleville Ball, showing Silver (Ag), Cadmium (Cd), Tin (Sn) and Antimony (Sb).

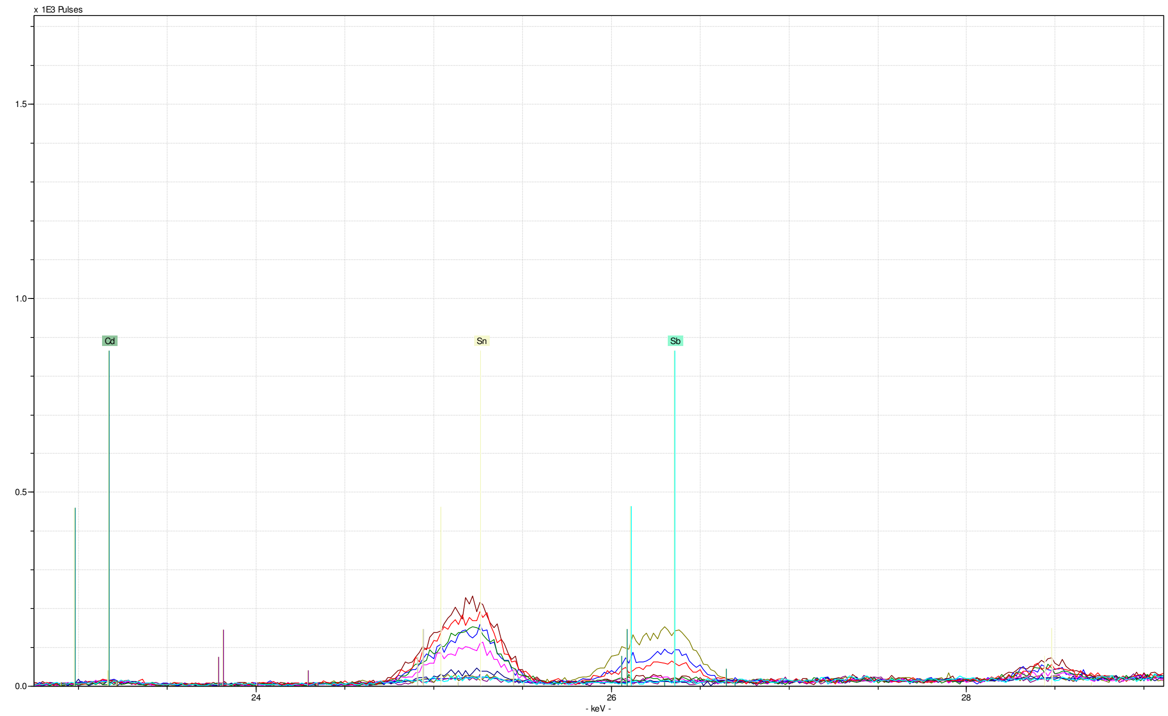

Figure 10. Spectra for Fusil Balls, showing Silver (Ag), Cadmium (Cd), Tin (Sn) and Antimony (Sb).

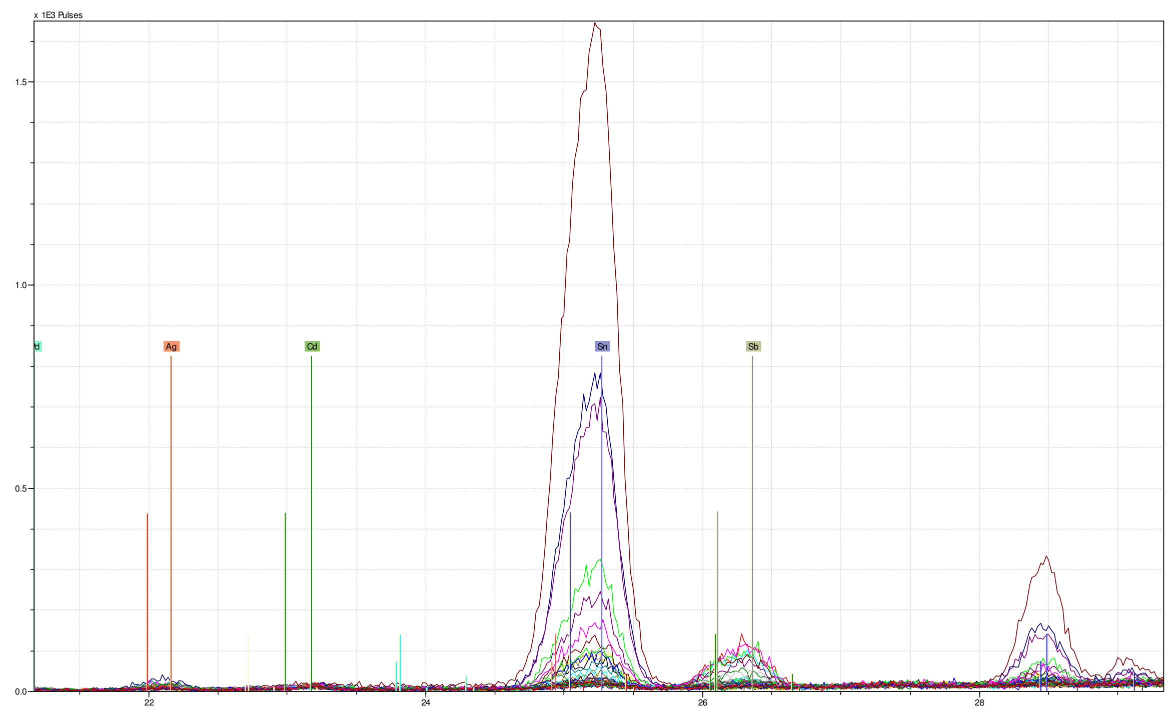

Figure 11. Spectra for Rifle Balls, showing Silver (Ag), Cadmium (Cd), Tin (Sn) and Antimony (Sb).

Antimony

Antimony (Sb) is a silvery white, brittle metalloid with the atomic number 51 (Butterman and Carlin 2004; Royal Society of Chemistry 2017). It occurs with lead ores. Antimony has a high melting point (1170°F) compared to lead. It has a value of 3 on Mohs hardness scale. In early America, Antimony was a key minor ingredient in the alloy pewter. It served to harden and strengthen the pewter.

Antimony photons (SbK12) values by weapon type were examined, which revealed British Standard, 82; Charleville, 433; Fusils, range from 23 to 3146, average 753; and Rifles, range from 24 to 2265, average 365. Antimony is lower in the British Standard ball compared to other weapon types at Kettle Creek.

Cadmium

Cadmium (Cd) is a soft, ductile metal with the atomic number 48 (Butterman and Plachy 2004; International Cadmium Association 2017). Cadmium occurs as an impurity in lead ores. Cadmium has a melting point of 610°F, which is slightly lower than that of lead. It has a value of 2 on Mohs hardness scale.

Cadmium photon (CdK12) values by weapon type were examined, which revealed British Standard, 136; Charleville, 195; Fusils, range from 52 to 157, average 127; and Rifles, range from 68 to 249, average 154. Cadmium does not appear to be a significant element for distinguishing between weapon types at Kettle Creek.

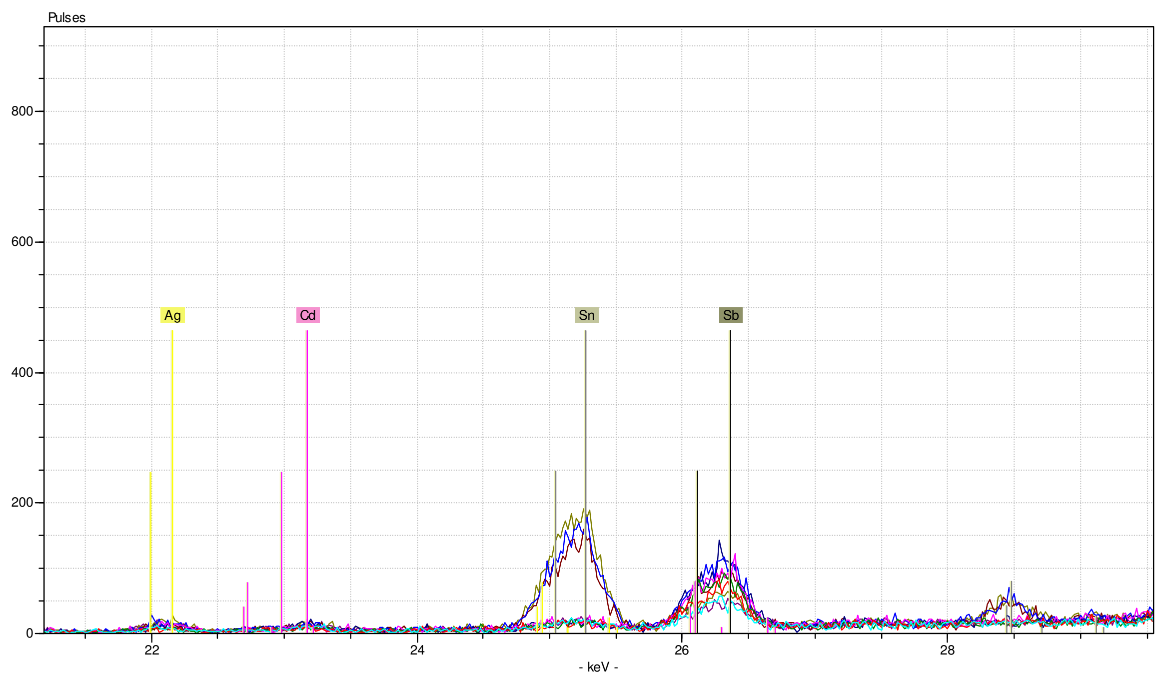

Figure 12. Spectra of 10 Samples with Higher Antimony (Sb) (Above 500 energy units in Sb K12).

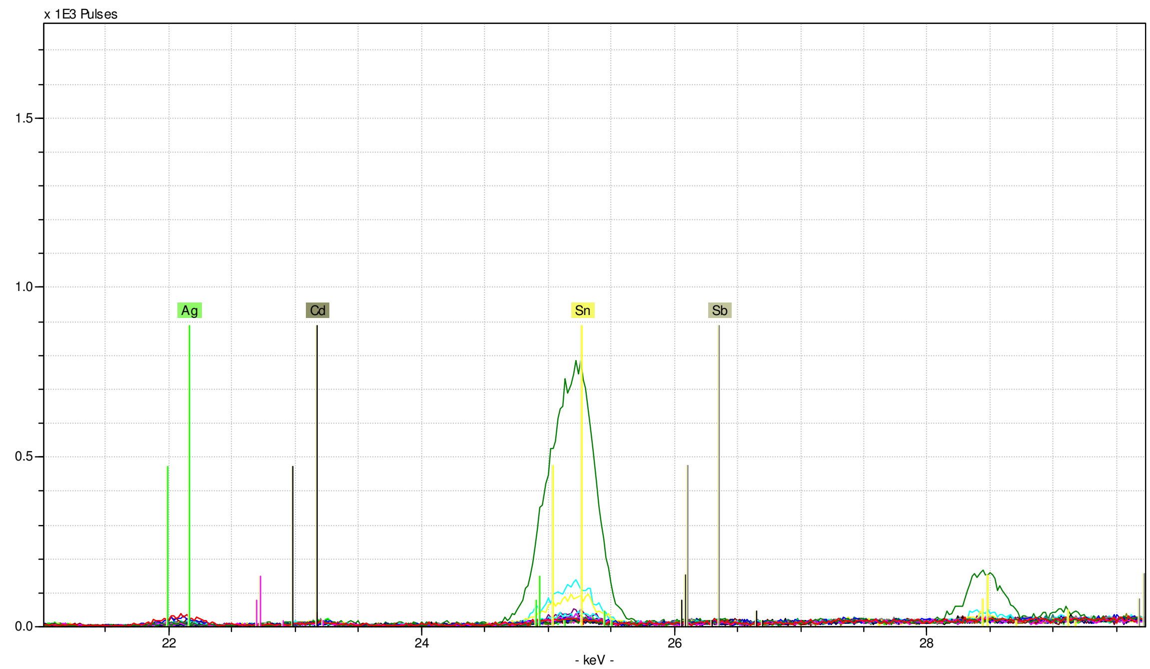

Figure 13. Spectra of 23 Samples with Lower Antimony (Sb) (Less than 100 energy units).

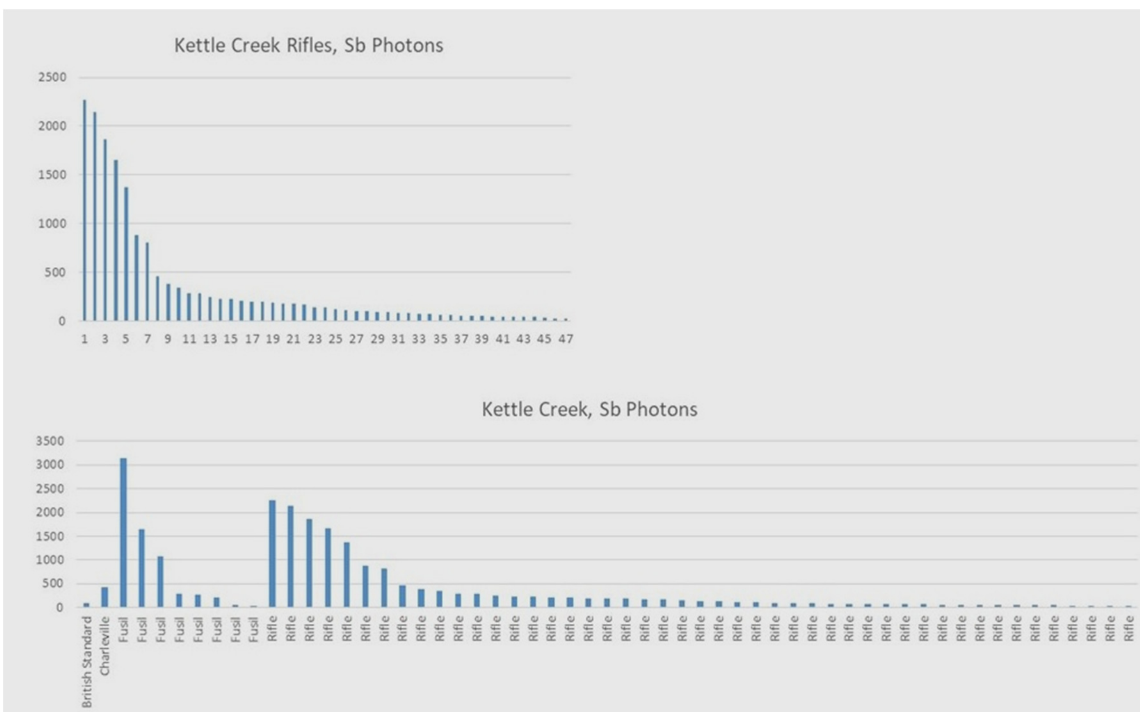

Figure 14. Graph of Antimony (Sb) Photons in Kettle Creek Sample.

Copper

Copper (Cu) is a malleable reddish-gold metal with the atomic number 29 (Doebrich 2009:1-4). It occurs with lead ores. Copper has a very high melting point (1984°F) compared to lead. It has a value of 3 on Mohs hardness scale.

Copper photon (CuK12) values by weapon type were examined, which revealed British Standard, 21; Charleville, 4; Fusils, range from 6 to 116, average 35; and Rifles, range from 1 to 52, average 18. Copper does not appear to be a significant element for distinguishing between weapon types at Kettle Creek.

Hafnium

Hafnium (Hf) is a lustrous, silvery gray, transition metal with the atomic number 72. It was not discovered until 1923. Hafnium has a melting point of 4051°F. It has a value of 5.5 on Mohs hardness scale (Greenwood and Earnshaw 1997).

Hafnium photon (HfL1) values by weapon type were examined, which revealed British Standard, 375; Charleville, 380; Fusils, range from 278 to 460, average 372; and Rifles, range from 219 to 449, average 363. While we are dealing with a very small sample size, Hafnium does not appear to be a significant element for distinguishing between weapon types at Kettle Creek.

Nickel

Nickel (Ni) is a silvery-white lustrous metal with the atomic number 28 (Nickel Institute 2017). Nickel has a very high melting point (2646°F) compared to lead. It has a value of 4.0 on Mohs hardness scale.

Nickel photon (NiK12) values by weapon type were examined, which revealed British Standard, 127; Charleville, 123; Fusils, range from 89 to 169, average 120; and Rifles, range from 63 to 175, average 123. Nickel does not appear to be a significant element for distinguishing between weapon types at Kettle Creek.

Silver

Silver (Ag) is a precious silver metal with the atomic number 47 (Butterman and Hilliard 2004). Silver has a high melting point (1761°F) compared to lead. It has a value of 2.5 on Mohs hardness scale. It commonly occurs with lead ores.

Silver photon (AgK12) values by weapon type were examined, which revealed British Standard, 78; Charleville, 152; Fusils, range from 94 to 355, average 188; and Rifles, range from 49 to 539, average 131. Silver appears to be less common in the single British Standard ball versus other weapon types at Kettle Creek.

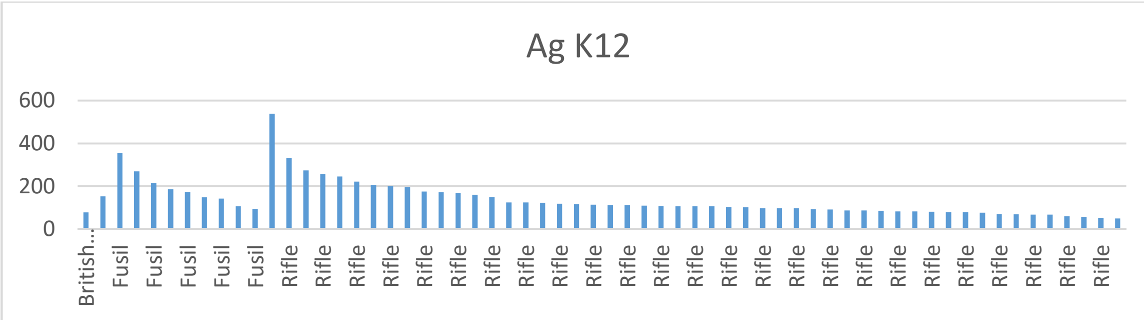

Figure 15. Graph of Silver (Ag) Photons in Kettle Creek Sample.

Tin

Tin (Sn) is a soft, white metal with the atomic number 50 (Calvert 2002). It occurs with lead ores. Tin has a melting point of 449°F, which is lower than that of lead. It has a value of 1.5 on Mohs hardness scale. Tin is a major component of pewter alloy.

Tin photon (SnK12) values by weapon type were examined, which revealed British Standard, 445; Charleville, 4808; Fusils, range from 298 to 4496, average 1982; and Rifles, range from 198 to 35,661, average 2098. Tin is less common in the single British Standard ball versus other weapon types at Kettle Creek.

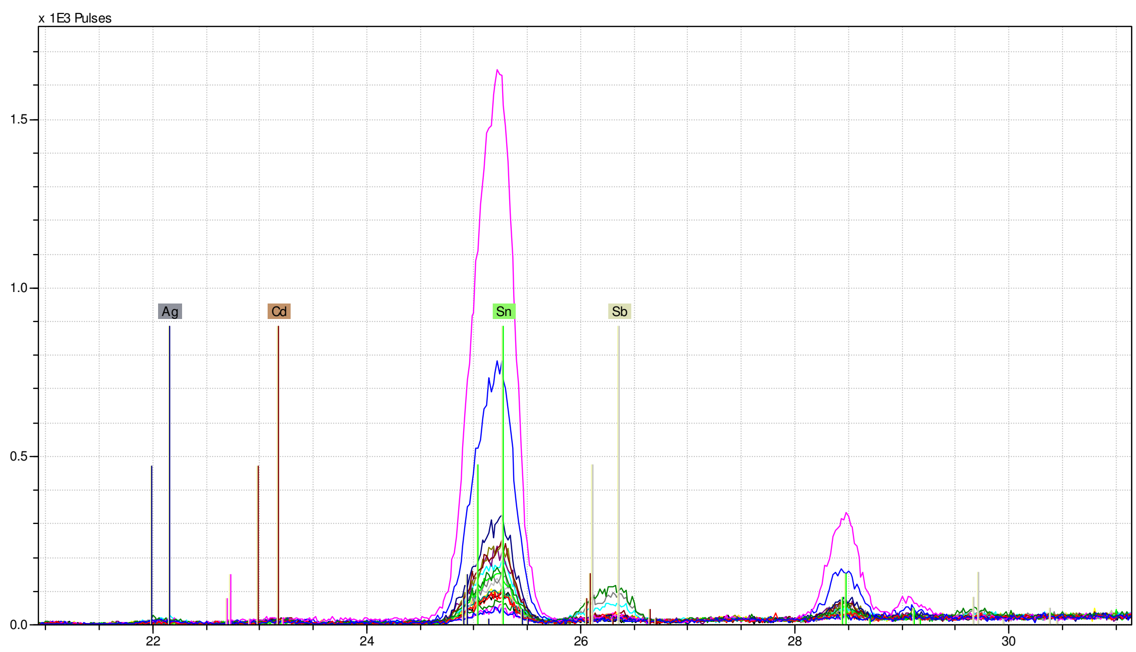

Figure 16. Spectra of 20 Samples from Kettle Creek with Higher Tin (Sn) (Energy levels greater than 500).

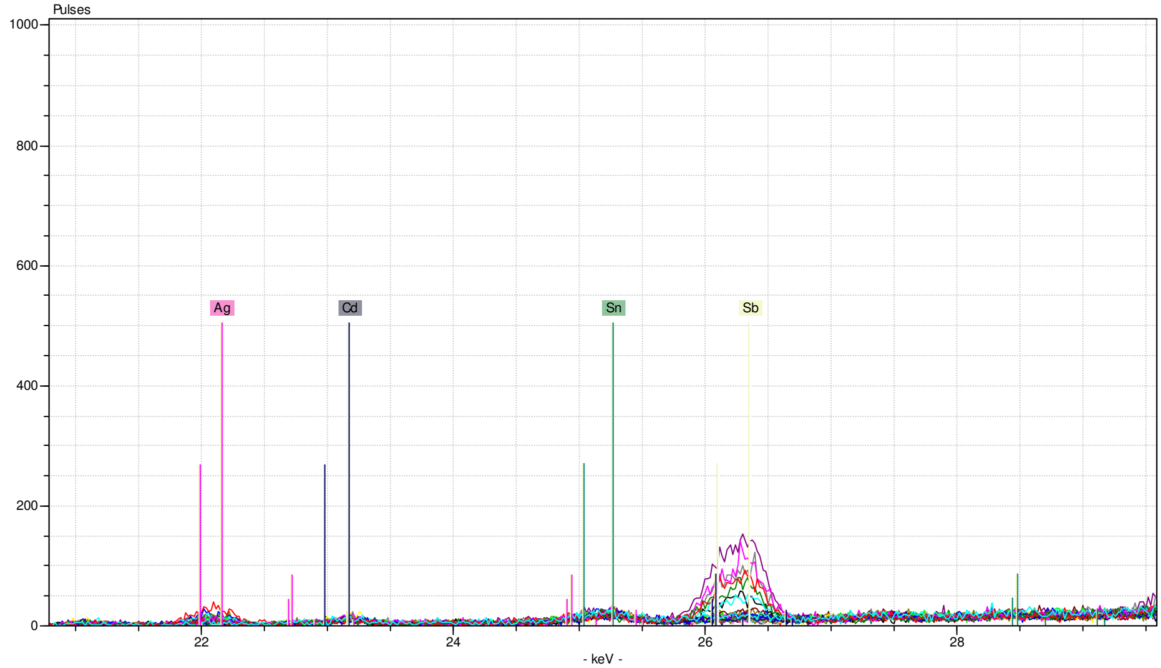

Figure 17. Spectra of 24 Samples from Kettle Creek with Lower Tin (Sn) (Less than 300 energy units).

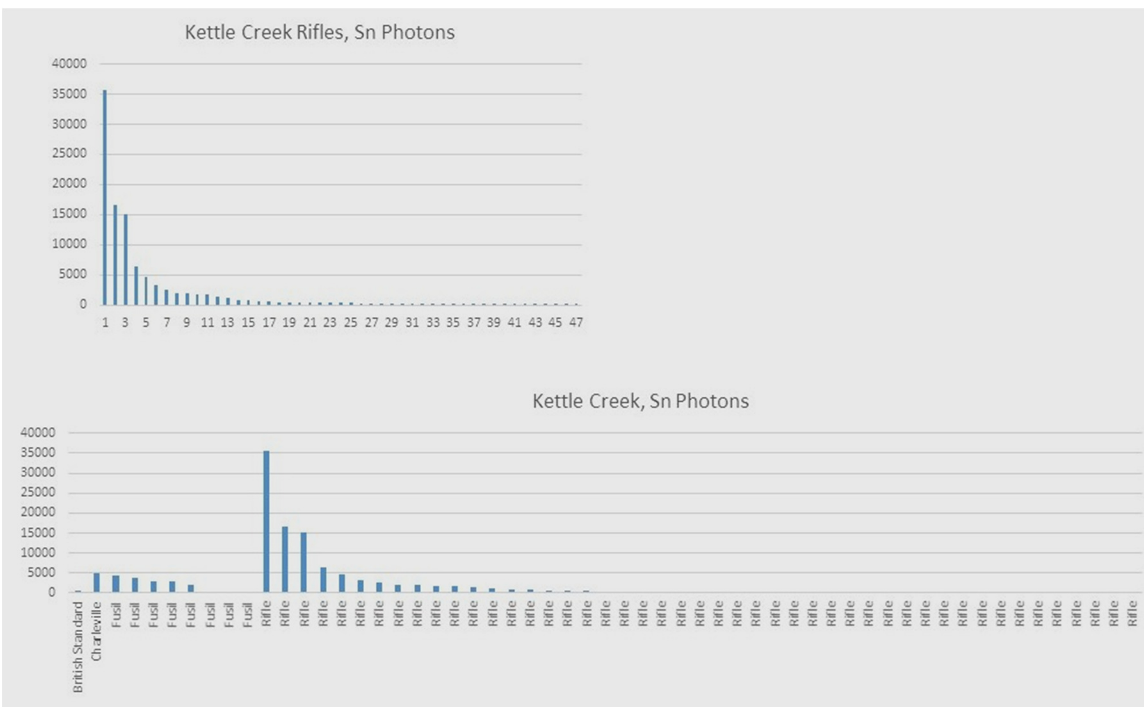

Figure 18. Graph of Tin (Sn) Photons in Kettle Creek Sample.

Zinc

Zinc (Zn) is a lustrous metal with the atomic number 30 (Bleiwas and diFrancesco 2010; International Zinc Association 2017). It is found with lead ores. Zinc has a high melting point (787°F). Zinc has a value of 2.5-3 on Mohs hardness scale.

Zinc photon (ZnK12) values by weapon type were examined, which revealed British Standard, 39; Charleville, 38; Fusils, range from 3 to 77, average 43; and Rifles, range from 0 to 212, average 41. Zinc does not appear to be a significant element for distinguishing between weapon types at Kettle Creek.

Zirconium

Zirconium (Zr) is a lustrous, grey-white strong transition metal with the atomic number 40. It has a melting point of 3371°F. It has a value of 5.0 on Mohs hardness scale (Greenwood and Earnshaw 1997).

Zirconium photon (ZrK12) values by weapon type were examined, which revealed British Standard, 556; Charleville, 463; Fusils, range from 377 to 599, average 487; and Rifles, range from 329 to 887, average 502. Zirconium does not be appear to be a significant element for distinguishing between weapon types at Kettle Creek.

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