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Analysis of Ammunition by X-Ray Fluorescence

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Abstract

Nondestructive analysis of lead shotgun pellets by X-ray fluorescence (XRF) shows considerable promise in assignment of the identity of the ammunition source. X-ray fluorescence spectra of various shotgun pellets and of standard alloys were obtained using an energy-dispersive instrument and an Am-241 source. The correlation obtained between the percent antimony in the standard alloys and the intensity of the K_{α} fluorescence peak from antimony was excellent. Peak areas from antimony in shotgun pellets were measured and compared to calibration plots from the standard alloys. The method was capable of distinguishing among lead-based alloys, such as ammunition, with antimony content as high as 10%.

Introduction

X-ray fluorescence (XRF) has become a standard method of analysis over the past 25 years (Leyden, 1987) and has been used for many years in analysis of ammunition (Brunelle et al., 1970). A principal advantage of XRF analysis is that there is often no need to dissolve the sample, to remove interferences, or other-wise to prepare the sample. Measurements can even be made directly on solid samples. While XRF measurements will not reveal the particular chemical forms of the elements present, simultaneous determination of the amounts of several elements is possible as long as the peaks do not overlap in the XRF spectrum. The intensity (peak area) of the fluorescent radiation from a given element varies somewhat according to texture, particle size, and the matrix in which the element is found. However, adjustments in the way a sample is prepared or in the way the data are interpreted can ameliorate those effects (Jenkins et al., 1981).

The principal elements present in leaded ammunition are lead, tin, and antimony. Lead shotgun pellets contain between 0.5% and 8% antimony, but very little tin (Grayson, 1984). Lead shot manufactured by Federal Cartridge Co. (Anoka, Minnesota) contains between 1.5% and 6% antimony, with higher percentages for more expensive loads (Gronfor, 1994). X-ray fluorescence analysis could be the method of choice for ammunition, since significant peaks for antimony, tin, and lead fall in the range of 10-30 keV and there is little interference due to overlap of peaks. This study was undertaken to determine whether direct measurement of the XRF peaks from lead or antimony could provide a rapid, reliable method of determining the composition and identity of lead shotgun pellets.

Materials and Methods

A 100-millicurie americium-241 source (Amersham Corporation, Arlington Heights, Illinois), placed in a lead cylinder to shield the operator from radiation, was used as the exciting source. An energy-dispersive X-ray fluorescence instrument (EG&G ORTEC, Oak Ridge, Tenn., Model # 7016-6165) with a Si-Li detector was used to measure the XRF signals. The system included a preamplifier, a 30 L liquid nitrogen Dewar, a 0.0127 mm thick beryllium detector window, and the Si-Li crystal diode (6 mm thick by 30 mm² area) centered about five cm below the surface of the sample position.

Shotgun pellets of different size and from different suppliers were obtained. Alloys of known composition (purchased from Brammer Standard Company, Houston, and National Institute of Standards and Technology, U.S. Dept. of Commerce, Gaithersburg, Maryland) were used for calibration of the method. Alloys were chosen so their composition encompassed the percentages of antimony expected in the shotgun pellets. The composition of these standards is given in Table 1.

Spectra of the standard alloys and the shotgun pellets were taken by exposing the samples to the radiation from the Am-241 source. Small plastic cuvettes with bottoms made of thin mylar film were used to hold granular samples. Acquisition and manipulation of data were facilitated by software provided by EG&G ORTEC. Command files were written and executed to collect XRF spectra for each sample. Assignment of peaks was made according to reference tables (Johnson and White, 1985). Computer programs were written to extract data from the "channel files" that the software created. A commercial program, QuattroPro (version 5.0), was then used to perform a regression analysis (correlating peak intensity and com-

position) and to generate the graphs shown below.

Table 1. Composition of standard alloys.

Standard Alloy and Description	Elemental Composition (%)		
	Lead	Tin	Antimony
"Lead Setting Up Sample" Cylinder Brammer Cat. # RPB15/5	64	30	1.6
"Lead Base Alloy" Granules Brammer Cat. # GBW2401	65.72	15.97	16.09
"Lead Base Alloy" Granules Powder Brammer Cat. # GBW2402	76.22	5.69	15.02
"Lead Base Bearing Metal" Cylinder NIST Cat. # 1132	83.7	5.84	10.26
"Lead Base White Metal" Small Granules Brammer Cat. # 177/2	84.5	5.07	10.10
"Hard Lead" Cylinder Brammer Cat. # IMN-PE1	99.36	0.59	0.053
"Hard Lead" Cylinder Brammer Cat. # IMN-PE2	99.27	0.50	0.27
"Hard Lead" Cylinder Brammer Cat. # IMN-PE3	99.13	0.38	0.49
"Hard Lead" Cylinder Brammer Cat. # IMN-PE4	98.99	0.31	0.70
"Hard Lead" Cylinder Brammer Cat. # IMN-PE5	98.90	0.21	0.89
"Hard Lead" Cylinder Brammer Cat. # IMN-PE6	99.07	0.40	0.53

Results and Discussion

A portion of the XRF spectrum of one of the "hard lead" standards (Catalog No. IMN-PE6 from Brammer Standards Co.) is given in Fig. 1. The spectrum was obtained by irradiation of the alloy for one hour. The vertical scale for the plot was chosen in order to expand the important fluorescence peaks from tin and antimony. Table 2 gives the assignment of the peaks of interest for lead, tin, and antimony.

Figure 2 gives the XRF spectrum of a particular sample of shotgun pellets (#6 shot from a 12 gauge Remington shell). As expected, comparison of the XRF spectrum of the shotgun pellets to that of the standard in Fig. 1 shows that the relative size of the peak for antimony has increased, while no peak occurs for tin in the spectrum of the shotgun pellets.

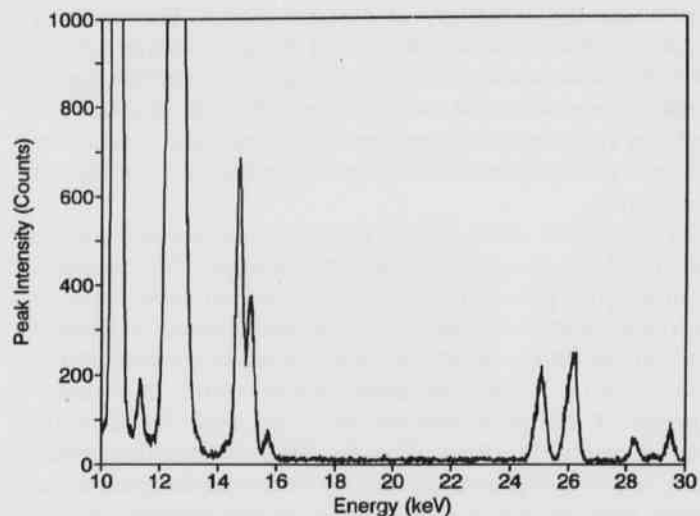


Fig. 1. X-ray fluorescence spectrum of lead alloy IMN-PE6.

Table 2. Peak assignment for XRF spectra of Pb, Sn, Sb alloys.

Energy (keV)	Assignment
10.6	lead - $L_{\alpha 1}$
12.6	lead - $L_{\beta 1}$
25.2	tin - $K_{\alpha 1,2}$
26.3	antimony - $K_{\alpha 1,2}$

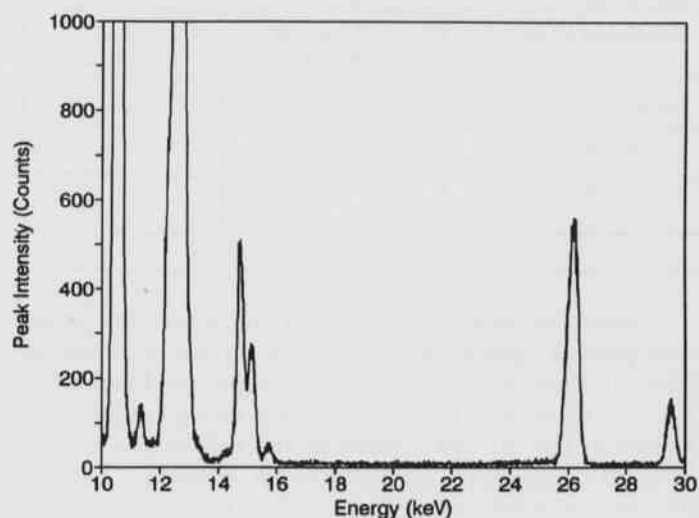


Fig. 2. X-ray fluorescence spectrum of remington #6 shot.

Ten spectra were taken for each sample in order to determine the reliability of measurements. The areas of peaks of interest were calculated for each sample from the ten spectra taken, along with averages of the areas. Typical standard errors were about 1% of the average values and repeated measurements after an interval of many months gave values in close agreement (less than 2% difference).

Peak areas were found to vary considerably as the nature of the sample's surface was changed. For example, compressing pellets into a disk caused all peak areas to increase. Such a behavior is entirely expected, since a greater surface area of the disk will be irradiated by the source and a larger fluorescence will result. As a consequence of this phenomenon an error arises in comparison of peak intensities between samples of different texture (e.g. - using a calibration plot prepared from standards that are metal cylinders to predict composition of shotgun pellets). In order to compensate somewhat for differences in sample texture, peak areas were scaled so that the elastic scattering (Rayleigh peak at 59.5 keV) from each spectrum had a value of 10,000 "counts." Table 3 compares "scaled" and "unscaled" areas for the antimony peak (26.3 keV) in one sample. Although the scaled value still differs from the value obtained for the compressed disk by about 10%, such an agreement is sufficiently close to distinguish many different shotgun pellets. Table 4 gives average areas and scaled areas for each of the standards. Ten spectra were obtained for each sample.

Table 3. Comparison of "scaled" and "unscaled" areas with changes in texture.

Remington #9 Shot	"Unscaled" Peak Area	"Scaled" Peak Area
Pellets	32,828	29,350
Compressed Disk	43,604	32,450
Percent Difference	25%	10%

Scaled and unscaled areas for the antimony peaks were plotted against percentages of antimony (listed in Table 1). Each gave an excellent straight-line fit (correlation coefficients > 0.9997). The plot using scaled areas (shown in Fig. 3) was chosen as the calibration plot in order to compensate for differences in texture of samples, as described above. The standard error (uncertainty in the value for area) according to the regression analysis was 1540 counts, a vertical distance on the plot which is less than half the height of the filled triangle marker.

Table 4. Intensities of peaks in standard alloys.

Sample Description	Average Area (59.5keV)	Scaled Area (59.5keV)	Average Area (26.3keV)	Scaled Area (26.3keV)
Brammer RPb 15/5	12,309	10,000	33,255	27,017
Nist 1132	13,101	10,000	220,315	168,167
Brammer 177/2	13,025	10,000	211,095	162,069
Brammer IMN-PE1	13,858	10,000	1,405	1,014
Brammer IMN-PE2	13,913	10,000	5,260	3,781
Brammer IMN-PE3	13,738	10,000	9,306	6,774
Brammer IMN-PE4	13,797	10,000	12,526	9,079
Brammer IMN-PE5	13,740	10,000	15,968	11,622
Brammer IMN-PE6	13,687	10,000	10,237	7,479

Inspection of Fig. 3 reveals the clear correlation of percent antimony with peak areas and, even though the available standards did not have percentages of antimony distributed evenly across the range of 0-10%, one expects the correlation to hold well throughout that range. In contrast, peak intensity at 12.6 keV could not be correlated well with percent of lead present. A plot of peak areas for lead (12.6 keV) versus percent lead for a number of standards is given in Fig. 4. Poor correlation may be due to a "saturation" that has occurred at higher concentrations. That is, a large concentration of lead present is quite efficient at absorbing the radiation, such that the amount of radiation absorbed does not increase linearly with increasing concentrations of lead.

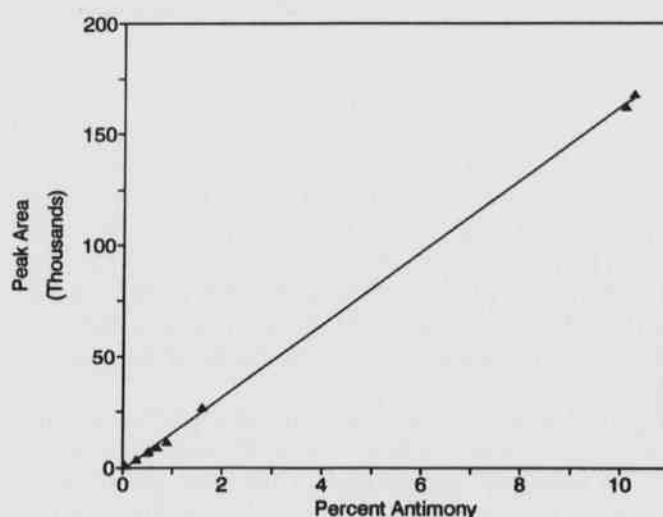


Fig. 3. Calibration plot of percent antimony vs. peak areas.

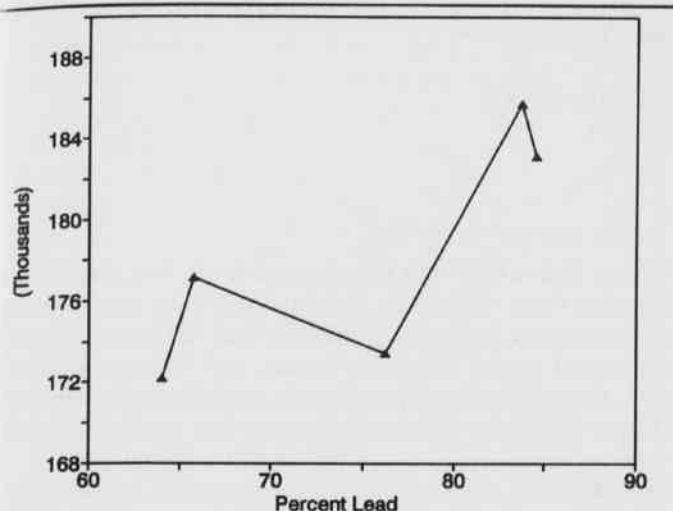


Fig. 4. Peak area from lead (12.6 keV) vs. percent lead.

Several different shotgun pellets were examined. The shot were donated by individuals or retail stores and were not identified other than by brand and shot size. The scaled areas of peaks from these shot are shown in Table 5, along with the percentages of antimony as predicted by the calibration plot.

Table 5. Comparison of spectra - shotgun pellets.

Sample Description	Pb Peak (12.6keV)	Sn Peak (25.2keV)	Sb Peak (26.3keV)	Percent Antimony
Federal No. 2	164463	0	8405	0.58
Peters Buckshot	160710	0	1523	0.16
Winchester No. 7.5	159620	0	17244	1.12
Remington No. 6	162167	0	22441	1.44

For these pellets, XRF measurements can clearly distinguish samples on the basis of peak intensity for antimony. According to information from Federal Cartridge Company (Gronfor, 1994), the less expensive shot ("promotional loads") have a lower percent antimony than the more expensive shot ("target loads"). Based on this information, the shot used in this study were likely the less expensive "promotional loads."

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