

Summary:

Isotope ratio analysis can be a valuable tool in cases where major and trace element analysis does not produce an unambiguous result. In the case presented here initial elemental analysis on a pullover belonging to a suspect from a shooting incident had shown increased lead and barium contents but also other metals. The defense argued that the contamination of the pullover was not due to the shooting incident but due to exposure in a metal workshop. Additionally the pullover had been kept under suboptimal conditions for several years. In order to determine if the lead on the pullover could originate from the shooting incident we studied the lead isotopic composition of different sections of the pullover and compared those with the lead isotopic composition of gunshot residues (GSR) recovered from the victim.

Introduction:

Different from the absolute concentration of an element, isotopic ratios retain a signature from the source of the element. Especially the lead isotopes are unique because the three radiogenic isotopes (^{206}Pb , ^{207}Pb and ^{208}Pb) and one stable isotope (^{204}Pb) allow the construction of several different isotope ratio scatter diagrams which permit a very sensitive and discriminative assessment of the possible different sources of the lead. In a ratio scatter diagram, where the two ratios share a common denominator, any mixing or contamination of different lead sources will show up as straight mixing lines.

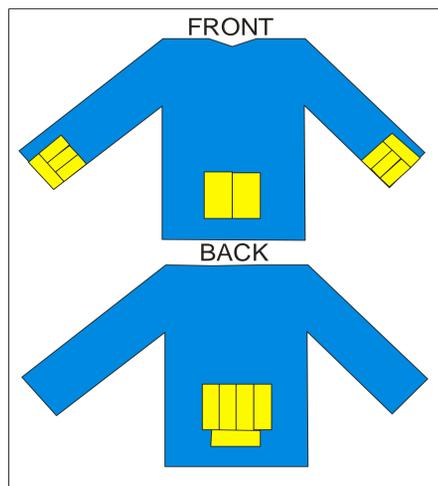


Figure 1. "Map" of sampled sections of the pullover.

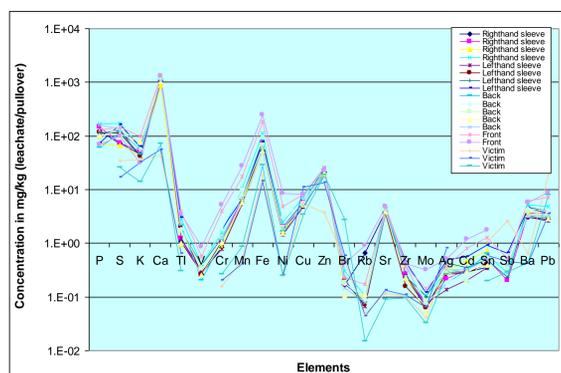
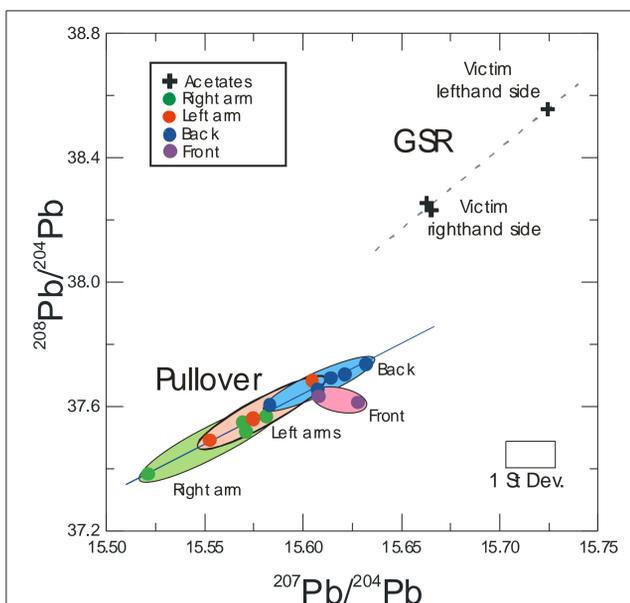


Figure 2. "Spidergram" of concentration of elements in leachate expressed as mg per kg of pullover.

In figure 2 the elemental analysis results are plotted in a "spider plot" to demonstrate the typical profiles of the pullover and the GSR retrieved from the sheets.

The lead isotope results are plotted in a $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ ratio scatter plot. Clearly there is no overlap of lead isotope ratios between those found on the pullover and those from the GSR. The front section is contaminated with a third component but that component is not from the GSR studied.

Figure 3. The lead on the pullover has most likely three sources but none which is similar to the Pb retrieved from the victim.



Methods:

15 different sections of the pullover (fig 1) were selected and elements were extracted in 15% HCl (Merck Ultrapur) by immersion and shaking for 5 days. Two acetate sheets with gunshot residues from the victim were treated in a similar manner. The major and trace element composition was determined with Total-Reflection XRF (Atomika EXTRA II A Spectrometer) at the laboratories of the Upper Austria State Government. For the determination of the lead isotopic composition, lead was extracted from the leachates by cation exchange and then measured on a multi collector Thermal Ionization Mass Spectrometer at the Free University of Amsterdam in the Netherlands (by JH).

Discussion

The elemental analysis showed that the pullover is contaminated with metals but not typically GSR. In figure 4 the averages for the arms and front are presented normalized to the average of the back of the pullover in order to visualize the increased concentration of several elements on the front sections. Elevated Pb, Ba and Sb concentrations are usually used as indicators for the presence of GSR. Sb was below the detection limit in the leachates and Ba and Pb were not significantly more enriched than other metals, indicating a strong metal contamination but not necessarily from a GSR source.

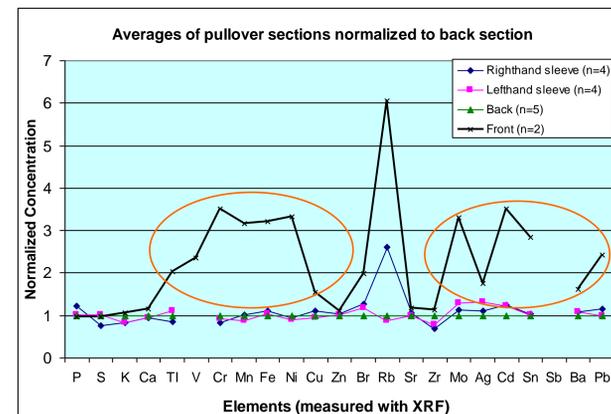


Figure 4. Normalized plot demonstrates the increased concentrations of several elements including Ba and Pb on the front section of the pullover.

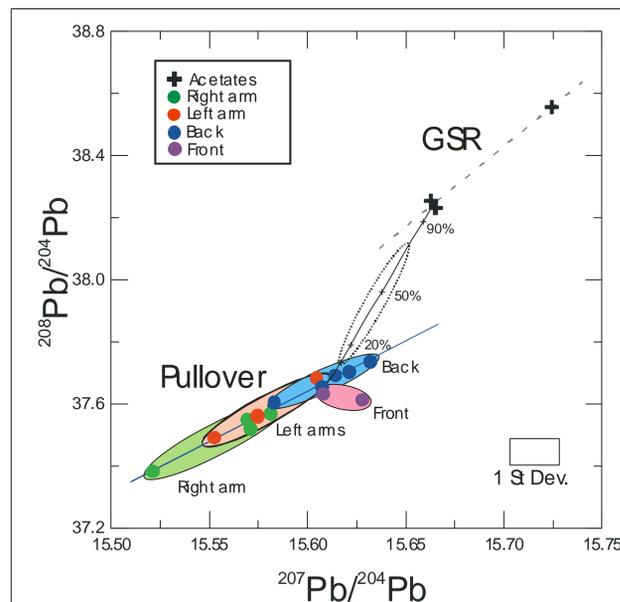


Figure 5. Calculated expected isotopic lead compositions if the pullover would have been contaminated with lead from the GSR.

The fact that lead has three isotopes, which each can have unique values, allows a very sensitive assessment of contamination of an item with lead from another source. Because the ratios in figure 5 have the same denominator any contamination of the pullover with lead from the GSR would have to produce some values on a "mixing line" which would connect the pullover and the GSR. As this is not the case it can be safely assumed that there is no GSR lead contamination of the pullover.

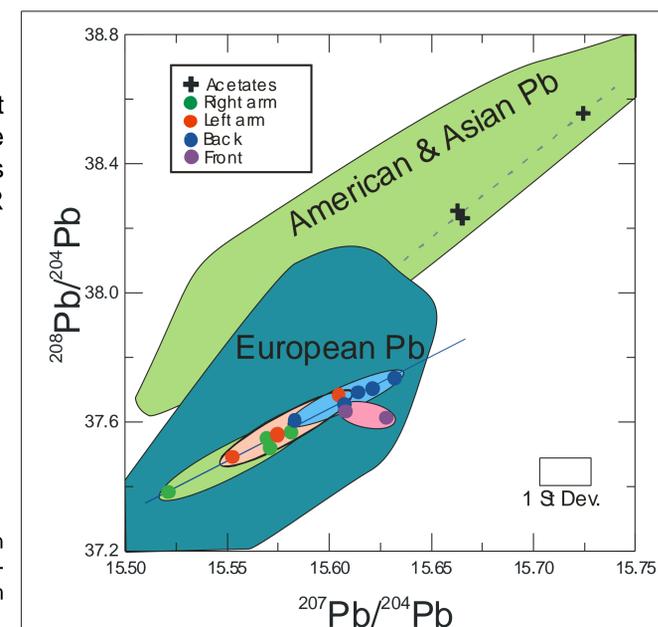
In figure 6 the results from the case are compared to regional lead isotope data which indicate that the lead on the pullover is probably from European origin but that the source of the Pb in the GSR might be non-European indicating projectiles of possibly American or Asian origin.

Conclusions

- Our study showed that at least three different sources contributed to the lead found on the pullover but that none of these three sources agreed with the composition of the GSR retrieved from the victim.

- The lead on the pullover is most likely from European origin but the lead from the GSR on the victim might be of a non-European origin.

Figure 6. Samples from the pullover seem to agree with an European origin where as lead from GSR appears to be non-European possibly American or Asian. (Fields from references 1,2 and 3)



Literature:

- Bollhöfer and K. J. R. Rosman. Isotopic source signatures for atmospheric lead: the Northern Hemisphere, *Geochimica et Cosmochimica Acta*, Volume 65, Issue 11, 1 June 2001, 1727-1740
- Bollhöfer and K. J. R. Rosman. Isotopic source signatures for atmospheric lead: the Southern Hemisphere, *Geochimica et Cosmochimica Acta*, Volume 64, Issue 19, 1 October 2000, 3251-3262
- Doë B. R. (1970) Lead isotopes. Springer Verlag, Berlin, Heidelberg, New York, pp. 137.