Text Control Material Analyses

Experimental (Outline)

I. Experimental approach – Comparable with Guinn's work. Adherence to general method, but inclusion of modern instrumentation, peak extraction methods.

II. Special concerns with bullet lead analysis. Potential for sample self-absorption; experimental and computational evaluation. Geometry concerns of small sample during irradiation and counting.

III. Sampling of bullet specimen. Three sampling protocols were followed - three samples per bullet; nine samples per bullet; nine samples with radial position recorded. Cutting technique, sample positioning and vial placement in irradiation container.

IV. Neutron activation analysis protocol

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   C. Irradiations and Counting: reactor description; irradiation facilities used, instrumentation description, acquisition and peak extraction software, specific timing protocol and reactions used, pneumatic work for silver, long irradiation for Sb, Cu, As

   D. Computation methods

V. Method Validation. QC results

VI. Uncertainty of results; budgeted uncertainty method and reproducibility plus bias method.

EXPERIMENTAL

Experimental approach

The analytical work performed in this study was designed to be comparable to the 1977 NAA work of Guinn [Anal. Chem., 51, No. 4, p. 484A, 1979]. Variations in the analytical protocol were made to accommodate the differences in the reactors used as well as counting instrumentation. Obviously, in the thirty years separating the experiments, significant advancements in detectors and electronics have been made. Perhaps most notably, modern computing has eased the incorporation of rigorous peak extraction methods and analytical corrections. Still, the basic implementation of the method in both cases was very similar and none of the improvements or modernizations is thought to be of such profound value that would discount the quality of the Guinn data. On the contrary, as is often the case, we recognize the exceptional quality of the data and marvel at the ability of early researchers to generate it under less optimal conditions.

Special concerns for bullet lead analysis

The bullet lead matrix poses special concerns during neutron activation analysis due to its heavy mass. The neutrons used as the analytical probe in this method find the lead sample to be fairly transparent but the gamma-ray which is emitted from the subsequent decaying nuclide of the element of interest is likely to be attenuated. Of course, elemental lead is generally used as the material of choice for shielding of gamma sources, so this is to be expected. In the case of the analysis of bullet material, the issue is to ensure that any self-absorption of the gamma-rays is minimized and if possible corrected for. Since the likelihood of absorption is based

on the path length of the emission through the sample as well as the absorption coefficient in lead, it is beneficial to use small samples.

Guinn used sample masses which varied from 1 to 50 mg. To a certain extent the sample masses were dictated by the fragments which were made available to him. The "stretcher" bullet was drilled and the resulting drillings/powder was analyzed. The inclusion of a powdered sample would add some complexity in any attempt to correct for sample self-absorption since the geometry might not be necessarily constant and it would be difficult to measure the dimensions of the sample.

In our studies, we found the small fragment chips we prepared from the bullet lead material weighing 15 to 20 mg had dimensions from as little as 0.1mm up to about 1.5mm, averaging perhaps 0.4mm. Assuming a particular gamma from a decaying nuclide of an element of interest was emitted in the direction of the detector from a location at the center of the fragment, the distance it would be required to traverse would average some 0.2mm. Based on gamma absorption coefficient tables [Nicholas Tsoulfanidis, Measurement and Detection of Radiation, Hemisphere Publishing Company, Washington, New York, London, 1983, page 556], loss of gamma intensity by absorption should average about 2.47 to 3.34% for the range of gamma energies utilized in this study employing this average distance. Because of the irregular geometries of the fragments we studied, we have elected not to make possibly inaccurate corrections to the data. Rather, we included considerations of self-absorption in the discussion of the bias contribution to our uncertainty estimates. In any event, our efforts to restrict sample masses to a small range should have resulted in minimized variations between bullet fragments due to this effect. It should

be noted, however, that Guinn's sample mass range would have resulted in significant absorption differences between samples, which could have been difficult to correct for.

Sample positioning in the neutron flux and counting positions is critical. The use of the exceptionally small samples required to minimize self-absorption resulted in the need for additional measures to ensure the sample was always held at a precise location in the sample irradiation package. Sample packaging will be discussed in more detail later.

Sampling of bullet specimen

Sample portions of 15 to 20mg were selected from the test bullets according to three different protocols. Three samples were prepared for ten bullets from each of lots 6000 and 6001, for a total of 60 samples. These bullets were already cut into large pieces, usually three to five, when received. No information was available as to the original location of the pieces within the bullet. Our intention was to take the samples from different parts of the bullet, so we cut them from the middle of three of these large pieces. When the base and nose of the bullets were identifiable parts of the pieces, we chose those pieces to sample, thereby ensuring the widest distribution of samples along the bullet length. Ten bullets from lot 6003 were sampled in a similar fashion, except three samples were removed from each of the three locations chosen for a total of nine samples per bullet or 90 for the lot. Finally, several bullets (bullet numbers 1, 8, 9 and 10) from lot 6003 were sampled a second time. At each of the three sampling locations of these bullets, the three samples were taken from an interior slice with one sample representing the radial center of the bullet (inside), one

representing the middle and one near the outside surface of the bullet (outside). The total number of samples prepared from lot 6003 bullets was 130.

Samples were removed from the bullet pieces by slicing through the cross section of the barrel of the bullet with a stainless steel knife. In each case, only interior lead material was selected by sectioning the slice to produce a fragment of the appropriate size. Lead samples were rinsed repeatedly in water and acetone, and then dried overnight under a heat lamp.

Samples were weighed into small polyethylene vials [EP1539LG, L&A Plastic Molding, Yorba Linda, CA] with inside diameters of about 4mm. The small sample vials were in turn encapsulated into standard 2/5 dram irradiation vials [EP338NAA, Emerald Plastics, Yorba Linda, CA] with appropriate spacers to ensure the small vials were held in the axial center of the irradiation package. This complex packaging was required to minimize possible lateral displacement of the small sample chips inside the larger vials. Sample weights were taken on our automated balance [AX205, Mettler-Toledo, Columbus, OH] using in-house-written software to create files which could be uploaded to our acquisition computer. This allowed for hands free balance operation and avoided potential errors in transcribing weights.

Neutron activation analysis

Standardization - Commercial plasma solutions were used for comparator NAA standards [Alfa Aesar, Specpure Plasma Standards, Ward Hill, MA]. Standards were prepared by depositing, and then drying, weighed portions of liquid solutions of known concentrations of the elements of interest into irradiation vials prepared exactly as for the bullet samples. Silver standards were prepared separately with

approximately two micrograms of element deposited into each standard. Composite standards were prepared for arsenic, antimony and copper by depositing about 6, 19 and 12 micrograms of these elements, respectively.

Quality material selection - Standard Reference Material Bullet Lead, SRM C2416 produced by National Institute for Standards and Technology (NIST) [National Bureau of Standards, Certificate of Analysis, Standard Reference Material C2416, Bullet Lead, February 16, 1988, Gaithersburg, MD] is intended for use as a composition standard for optical emission spectrometric methods in which the entire standard is used whole. As such, it is not the best candidate for sectioning into samples of mass comparable to the samples in this study, and for use as a quality material to measure accuracy of the procedure and to estimate methodological uncertainty. Due to its intended use, for instance, no minimum sample mass is provided by NIST. However, no other reference material of similar matrix to the study samples was found available for this purpose, so the C2416 standard was used in our study. A total of 13 measurements were made for silver and 28 measurements were made for the other three elements. We fully recognize the difficulty of developing bias estimates based on this standard. To help alleviate this issue, we included three analyses of NIST SRM 1571, Orchard Leaves for arsenic [National Bureau of Standards, Certificate of Analysis, Standard Reference Material 1571, Orchard Leaves, January 28, 1971, revised August 15, 1976, Gaithersburg, MD]. In addition we included three analyses of a second independent set of plasma standards

(referred to in this manuscript as the TERL standards) from a different manufacturer for silver and six analyses for the other elements.

Irradiations and Counting - All irradiations were performed at Texas A&M University's Nuclear Science Center which operates a 1 MW T.R.I.G.A. research reactor. The facility's irradiation positions include a pneumatic tube and rotisseries, both with nominal neutron fluxes of 1 x 10^{13} $cm^{-2}s^{-1.}$

Silver was determined using the pneumatic facility by sequentially irradiating standards, unknowns and quality materials for 60s (T_i), followed by a 30s delay (T_d) and a 180s count period (T_c). The $^{109}Ag(n,()^{110}Ag$ reaction induced by thermal neutrons during the irradiation gave rise to the 657 keV gamma line ($E_($) from ^{110}Ag which decays with a 24s half-life ($t_{1/2}$). ^{108}Ag ($t_{1/2 =}$ 2.41m) is also produced but the 657 keV is the most intense silver gamma-ray, so it was used in the present study. The gammas were measured using a high resolution HPGE spectrometer [Ametek, Ortec EG&G, Oak Ridge, TN] with relative efficiency of 50% and resolution of 1.80 keV measured at the 1332 keV line of ^{60}Co. The detector is interfaced to a Genie-PC multichannel analysis system [Areva, Canberra Industries, Meriden, CT], via Canberra's digital pulse processor, DSP 2060, and acquisition interface module, AIM 556. After acquisition of all spectra for each days run, spectral files were transferred electronically to our alpha based ESP-Genie system located on campus, some 5 miles distant from the reactor center.

Arsenic, antimony and copper were each determined utilizing longer-lived isotopes, therefore a rotisserie irradiation was employed. Six of the unknown

samples, three composite standards, one bullet lead quality control sample and a blank vial were routinely packed into each rotisserie can. Six such cans, approximately 2.3in inside diameter and 1.4in height, were stacked into a rotisserie "long tube" and placed in to a near-core position. The device was rotated at a speed of about 3 revolutions per minute during the 2 hour irradiation period. Some seven irradiations were required to process all the samples studied in this work.

Irradiated materials were returned to our laboratory on campus for gamma spectrometry of long lived species. Neutron capture reactions were responsible for production of indicator isotopes ^{76}As ($t_{1/2}$= 26.4h, $E_{(}$=559keV), ^{122}Sb ($t_{1/2}$= 2.70d, $E_{(}$=564keV) and ^{64}Cu ($t_{1/2}$= 12.7h, $E_{(}$=511keV). The 511keV line from ^{64}Cu is the result of positron annihilation and therefore not necessarily specific for copper. The intensity of the 511 keV line is, however, much greater than for the 1346keV line, so it was used in this study, as it was for Guinn's work. Decay curves were constructed to ensure no significant contribution from other positron emitters affected the results. These gamma-rays were measured on one of two HPGE spectrometers: a Canberra, 42% relative efficiency with 1.74 keV resolution and an Ortec 25% relative efficiency with 1.68 keV resolution. Each of these is interfaced directly to our ESP-Genie system through AIM modules via either DSP or conventional analog pulse counting electronics. Samples were counted in irradiation batches with each irradiation can being processed in consecutive counts on a single detector system.

Computation - Peak area determinations and comparisons of unknown materials to standards were accomplished using the Canberra NAA Genie routines resident on the

alpha system. Run descriptor files were prepared and merged with weight data files which were electronically transferred between the sample preparation and data acquisition computer systems. Output files were merged with spreadsheets for tabulation and presentation of resulting data.

Method validation

Average results of analyses of quality control material SRM C2416 are presented in table 1. It can be noted that our results do differ from NIST certified values but in each case, the standard deviation of the distribution of results overlaps with the quoted uncertainty for the literature value. It must also be noted, however, that NIST specifies that the uncertainties for their certified values for this standard are not statistically derived measures of imprecision but are "based on judgment." In addition, again, we should caution that our use of this particular standard was not in compliance with the original intent for its production.

Table 1. Results for quality material, SRM C2416 (n=13 for Ag; n=28 for As, Sb, Cu).

	Elemental Concentration (ppm)							
	Ag		As		Cu		Sb	
	Conc.	Err.	Conc.	Err.	Conc.	Err.	Conc.	Err.
average	47.4		520		667		7720	
stdev	2.78		31.5		81.2		451	
literature/uncer	44	2	560	10	650	20	7900	100
%deviation	+ 9.79		- 6.86		+3.05		- 2.03	

Arsenic analysis of SRM 1571 resulted in an average concentration of 11.15 ± 0.61 μg/g which is 4.16% (relative) greater than the NIST certified value of 10.7 ± 1.3 μg/g. Again, one may note that errors overlap.

Finally, results of an independent set of solution standards [Inorganic Ventures, Lakewood, NJ], (referred to here as TERL standards) were analyzed as unknowns to provide an indication of accuracy. These data are tabulated in table 2. Note that these TERL standards have very low certified uncertainties. In the cases of silver and copper, the literature value is within standard deviations from the mean of our measurements. In every case the deviation of our mean result to the literature value is about 5.5% or better. It should be noted there that while the TERL standards are independent from the calibration standards, there is no reason to consider their certificate concentrations as more or less accurate. Therefore any consideration of method bias which is based on evaluation of these results as if they are of a known reference material is suspect.

Table 2. Results for quality material, TERL Stds (n=3 for Ag; n=6 for As, Sb, Cu).

	Elemental Concentration (ppm)							
	Ag		As		Cu		Sb	
	Conc.	Err.	Conc.	Err.	Conc.	Err.	Conc.	Err.
average	19.7		45.7		89.0		177	
stdev	0.23		0.67		1.07		3.28	
literature/uncer	20.84	0.04	47.67	0.10	89.553	0.18	186.87	0.37
%deviation	-5.54165		-4.0809		-0.57663		-5.4115	

Uncertainty of results

In recent years, estimation of measurement uncertainty has been somewhat standardized by the publication of procedures which are recognized as best practice. The utilization of the GUM methods ["Guide to the Expression of Uncertainty in Measurement," ISO, Geneva, 1993; ANSI/NCSL A540-2-1997, "US Guide to the Expression of Uncertainty in Measurement, First Edition, American National

Standards Institute, Washington D.C., 1997; Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST TN 1297, National Institute of Standards and Technology, 1994] requires the identification and evaluation of each potential component of uncertainty. Systematic error, or bias, is expected to be identified and eliminated or estimated and corrections of results made. Many methods, including neutron activation analysis, are sufficiently well understood and described mathematically to make use of the GUM "bottom-up" approach. In this case, we have a well understood, yet highly variable bias in the self-absorption of signal gamma-ray by the lead sample matrix. Because of the variability of geometric presentation of the irregular sample to the neutron beam and the detector, only a potential average bias was readily determined, so we included them in the uncertainty budgets. Table 3 is an example of a GUM compliant uncertainty budget based on bullet #1, lot 6003. The total computed uncertainty for silver, copper and antimony is 5.12%, 3.95% and 3.49% respectively. The high uncertainty of nearly 20% determined for arsenic is due to the low concentration of arsenic in that particular bullet. Bullet #3 from the same lot had much higher arsenic concentrations. The arsenic gamma peak area uncertainty component for bullet #3, for example, is less than 1%, resulting in a total uncertainty in line with the other elements of less than 4%.

Table 3. Unceratinty budget based on Bullet #1, Lot 6003.

Uncertainty Budgets	Ag	As	Cu	Sb
	Percent Std Dev			
Type A				
Gamma Counting Peak Areas	3.01	19.4	1.27	0.15
Std Yield Measurement	0.3	0.1	0.12	0.06
Repeatability (based on stds)	1.67	1.78	1.65	1.82
Reproducibility (not measured)	0	0	0	0
Sample Inhomogeneity (not measured)	0	0	0	0
Instrument Timing (based on 1 sec error)	2.85	0	0	0
Type B				
Comparator Standard Calibration	0.3	0.3	0.3	0.3
Density Variation (not included)	0	0	0	0
Self-absorption	2.47	3	3.34	2.96
Total Uncertainty (%)	5.12	19.71	3.95	3.49
(All sensitivities are estimated as 1)				

As discussed, in this case we have an uncorrected bias which is included, somewhat against GUM principles, in the budget as the average deviation of QC sample results from accepted values.

An alternative approach to estimating the overall uncertainty is through the use of measured precision combined with any uncorrected method bias. This "top-down" approach is formalized to some extent [Draft OSP TS 21748, "Guide to the Use of Repeatability, reproducibility and Trueness Estimates in Measurement Uncertainty Estimation," Geneva, 2003], yet is less well accepted. Application of this approach to our study would include measurement of reproducibility of reference material (SRM C2416) and its combination with of the average uncorrected bias for each element. The uncorrected bias is computed as the average percent deviation of quality material

(SRM C2416, SRM 1571 and TERL Standards) mean results from accepted values. Uncertainties computed in this way are presented in table 4.

Table 4. Computation of uncertainties using "top-down" approach.

Average Error (rel %)				
	Ag	As	Cu	Sb
SRM Φ	5.87	6.05	6.61	5.84
Average Bias	2.15	-2.27	1.25	-3.70
Combined Uncertainty	6.25	6.46	6.73	6.91

Depending on the method of uncertainty estimation, the overall uncertainties ranged from about 3.5 to 7% for each of the elements in the study with the exception of arsenic. Arsenic had similar uncertainties for those bullets with high (greater than 1 ppm) concentrations.