R. C. McFarland,[1] M.S. and M. E. McLain,[1] Ph.D.

Rapid Neutron Activation Analysis for Gunshot Residue Determination

A recent review of neutron activation analysis (NAA) applications in forensic science by Guinn [1] has again focused attention on the utility of barium and antimony determinations on residues removed from the hands as indication of recent gun firing by the individual. This method has been well established and is in routine use by state, local, and federal law enforcement groups in the United States and by governmental agencies in other countries. Increasing use of this technique has made reduction in sample analysis time imperative.

Due to inherent contamination by sodium and other contaminants of the paraffin casts or cotton swabs used to collect the residues for NAA, the purely instrumental NAA approach has not proven practical; and radiochemical separations must be performed on the irradiated samples prior to counting.

The activation products used as indicators of the barium and antimony contents of the casts or swab samples are ^{139}Ba and ^{122}Sb, respectively. Table 1 gives the pertinent decay characteristics of these radionuclides [2]. As can be deduced from the data presented in Table 1, the 165.8 keV gamma ray of ^{139}Ba and the 564.8 keV gamma ray of ^{122}Sb give the best sensitivity for detection and measurement for these nuclides in the NAA procedure.

The relatively short half-life of the ^{139}Ba penalizes the effective sensitivity of the NAA method when lengthy radiochemical separations are performed. The normal separation method for barium is the precipitation of the barium carrier as barium sulfate from a dilute aqua regia leach of the casts or swabs. This precipitation is rapid in itself, but the gravimetric carrier yield determination methods are very time consuming since they involve the pre-weighing of washed and dried filter papers and washing, drying, and weighing of the barium sulfate precipitate after collection on the filter papers prior to counting. Typically, a laboratory worker will require 90 minutes of processing time for a group of ten samples before the ^{139}Ba counting can begin. In this time more than half of the ^{139}Ba activity induced in the reactor irradiation has been lost.

The longer-lived ^{122}Sb does not suffer from significant decay during the subsequent separation precipitations (first as the sulfide, then as elemental Sb.). However, in both the Ba and Sb separations, the time consumed in gravimetric determinations of the carrier yield in the precipitate to be counted is considerable. This factor limits the analysis capacity of the laboratory worker and, therefore, increases the costs per analysis.

Some laboratories have been forced by the increasing sample load to abbreviate their radiochemical separations procedures by elimination of the yield determination steps. Failure to properly compensate for this chemical yield factor in the NAA post-irradiation

TABLE 1—*Decay characteristics of Ba and Sb nuclides.*

Isotope	Production Method	Half-Life	Gamma Ray Energies, keV	Absolute Intensity[a]
^{139}Ba	^{138}Ba(n,γ)^{139}Ba	82.9 min	165.8	22.3
			1254.8	0.03
			1310.6	0.02
			1420.5	0.31
^{122}Sb	^{121}Sb(n,γ)^{122}Sb	64.3 h	564.1	63.0
			692.8	3.27
			1140.6	0.66
			1256.6	0.65
^{133}Ba	^{132}Ba(n,γ)^{133}Ba	10.7 years	53.2	2.0
			79.6	3.45
			81.0	32.8
			160.7	0.62
			223.2	0.45
			276.4	7.32
			302.9	18.5
			356.0	63.0
			383.9	9.0
^{125}Sb	^{124}Sn(n,γ)^{125}Sn $\xrightarrow{\beta^-}$ ^{125}Sb	2.70 years	111.0	0.14
			117.3	0.37
			122.1	0.05
			172.0	0.29
			172.7	0.38
			176.3	9.05
			204.2	0.43
			228.7	0.15
			321.1	2.00
			380.6	1.70
			408.8	0.47
			428.0	42.7
			443.8	0.40
			463.4	13.5
			600.7	22.6
			606.8	7.80
			636.1	15.4
			671.4	2.4

[a] Gamma rays per 100 disintegrations.

separation procedures may, however, incur an undesirable uncertainty factor in interpretation of the results.

Members of the laboratory staff at the Georgia Tech Research Reactor (GTRR) have been cooperating with the Georgia State Crime Laboratory in the applications of such gunshot residue detection studies. In the course of this work an improved carrier yield measurement method has been developed. This radiometric yield determination technique is based on the incorporation of ^{133}Ba and ^{125}Sb as radioactive tracers into the barium and antimony carriers. ^{125}Sb is not produced in the thermal neutron irradiation of antimony and the quantity of ^{133}Ba induced in an irradiated sample is insignificant. The decay characteristics of these two nuclides [2] are also given in Table 1.

Provided that a high-resolution lithium-drifted germanium [Ge(Li)] detector is used in counting the separated samples, there is no interference between the mixed activities ^{139}Ba-^{133}Ba or ^{122}Sb-^{125}Sb. The energetically similar 160.7 keV gamma ray from ^{133}Ba does

not contribute significantly to the 165.8 keV gamma ray peak of ^{139}Ba due to the very low intensity of the ^{133}Ba gamma ray.

Since the NAA is accomplished by comparison to a standard sample of barium and antimony irradiated and processed in the same manner as the unknown samples, an absolute yield determination is unnecessary. Therefore, a simple comparison of the amounts of ^{133}Ba and ^{125}Sb in the separated samples against the separated standards is sufficient for the needed chemical yield correction. The data for the ^{133}Ba and ^{125}Sb activity is obtained from the same gamma ray spectra used to measure the ^{139}Ba and ^{122}Sb neutron activation products.

Experimental

Neutron Source

Georgia Tech Research Reactor (GTRR). One megawatt (thermal), heavy water cooled and moderated. Neutron flux used: 8×10^{12} neutrons cm^{-2} s^{-1}.

Gamma Ray Spectrometer

Fifty-four cc Ge(Li) detector coupled to Nuclear Data 2200 1024-channel pulse height analyzer. Spectrometer connected to Hewlett-Packard Model 9100B computer through Applied Physical Technology Model 2291 interface. The latter equipment permits on-line, rapid data processing.

Reagents

The tagged barium carrier solution was prepared by adding ^{133}Ba to an aqueous solution of Ba(NO$_3$)$_2$ containing approximately 20 mg/ml barium. The tracer concentration of the final barium carrier solution was adjusted to 0.34 μCi of ^{133}Na per ml. This specific activity was chosen to give good counting statistics when counting the final BaSO$_4$ precipitate on the 54 cc Ge(Li) detector. The tagged antimony carrier solution was prepared by adding carrier free ^{125}Sb to a solution of antimony metal in dilute aqua regia to give a solution containing approximately 20 mg/ml antimony and a ^{125}Sb concentration of 0.14 μCi/ml. A holdback carrier containing 5 mg/ml each of NaCl, KCl and MnCl$_2$ was used.

Procedure

The swabs or paraffin casts were individually sealed in polyethylene vials and irradiated in the GTRR for approximately eight hours along with a standard for comparison containing 10 μg each of barium and antimony. After irradiation each cast was leached by boiling for 10–15 min in dilute aqua regia to which 1 ml of each of the carrier solutions was added. BaSO$_4$ was precipitated from the decanted leachate by the addition of 1 ml of 18M H$_2$SO$_4$. The solution was centrifuged and the supernate set aside for the antimony determination. The precipitate was filtered and rinsed with water, methanol, and ethyl ether. For the purpose of comparison between the gravimetric and the radiometric methods of yield determination, the precipitate was dried, weighed, and counted for both ^{139}Ba and ^{133}Ba. Then, hydrogen sulfide was passed through the supernate from the BaSO$_4$ precipitation. The precipitated Sb$_2$S$_3$ was dissolved in 12 M HCl and chromous chloride solution added to precipitate antimony metal for weighing and counting. After rinsing, drying, and weighing, the antimony precipitate was counted for ^{125}Sb and ^{122}Sb.

Results

The experimental results from the comparison of the chemical yields determined by the conventional gravimetric means and by the radiometric method described in this paper are given in Tables 2 and 3. This data was obtained by the analysis of a group of eight actual paraffin hand casts. The chemical yields for the barium sulfate and the elemental antimony precipitation separations were determined by both methods. As shown in Tables 2 and 3, the agreement is excellent.

TABLE 2—*Relative Barium yield (STD1 = 100%).*

Sample	Radiometric Method, %	Gravimetric Method, %	Difference, %
STD1	100	100	...
STD2	69.9	69.9	0
SX1	101	100	+1
SX2	95.2	96.5	−1.3
SX3	106	107	−1
SX4	93.9	89.5	+4.4
SX5	114	113	+1
SX6	110	106	+4
SX7	100	98.1	+1.9
SX8	111	108	+3
Mean Difference	2.1%		
Standard Deviation	±1.4%		

TABLE 3—*Relative Antimony yield (STD1 = 100%).*

Sample	Radiometric Method, %	Gravimetric Method, %	Difference %
STD1	100	100	...
STD2	75.5	70	+5.5
SX1	70.2	82.4	−12.2
SX2	86.5	96.2	−9.7
SX3	88.1	90.6	−2.5
SX4	80.1	81.7	−1.6
SX5	76.9	71.1	+5.8
SX6	71.2	70.6	+0.6
SX8	97.6	96.5	+1.1
Mean Difference	−1.6%		
Standard Deviation	±6.5%		

Gamma ray spectra from actual separated barium sulfate and antimony precipitates are given in Figures 1 and 2.

Conclusions

The radiometric method of chemical yield determinations in the post-irradiation radiochemical processing of gunshot residue samples gives comparable values for the chemical separations yields for barium and antimony. Furthermore, the time required for the separations is reduced from the former 90 minutes to less than 30 minutes in the case of the barium determination. Later experiments have demonstrated that additional savings in
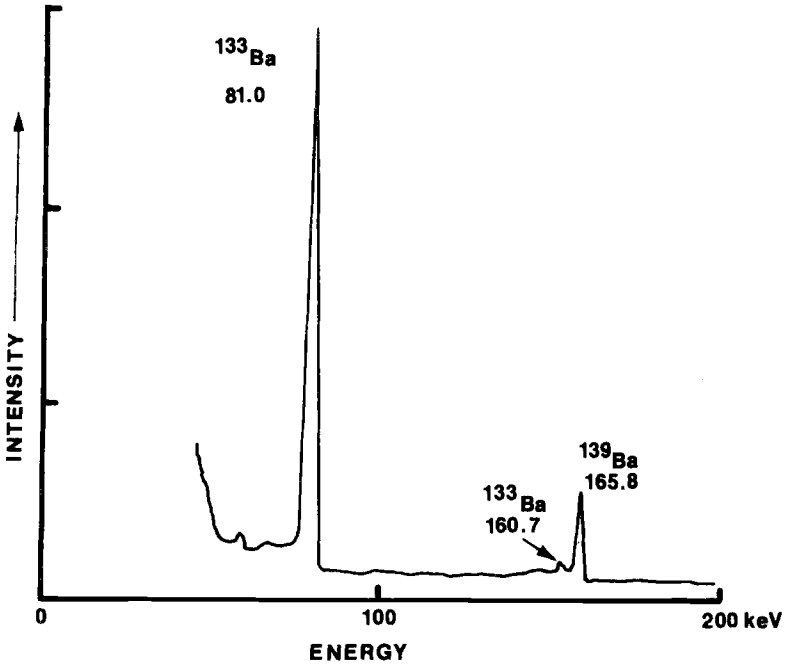
FIG. 1—*Typical gamma ray spectrum from BaSO₄ precipitated with ¹³³Ba-tagged barium carrier in post-irradiation chemical separation for gunshot residue NAA.*
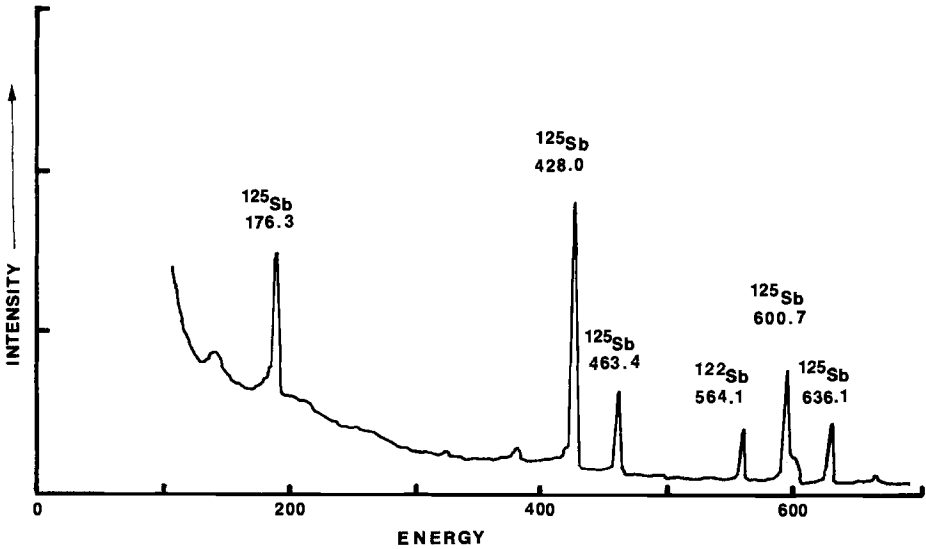
FIG. 2—*Typical gamma ray spectrum from Sb precipitated with ¹²⁵Sb-tagged antimony carrier in post-irradiation chemical separation for gunshot residue NAA.*

chemical separations time and effort can be realized by the centrifugation and direct counting of the Sb_2S_3 precipitate. The incorporation of the tagged carrier compensates for counting geometry differences between the standards and the unknowns when the precipitated Sb_2S_3 is counted in the centrifuge tube after decanting the supernate and washing the precipitate to remove contaminants. Nonradioactive contaminants (for example, elemental sulfur) do not influence the radiometric yield determination as they do the conventional gravimetric method.

References

[1] Guinn, V. P., *Isotopes and Radiation Technology, A Quarterly Technical Progress Review*, Vol. 9, No. 4, 1972, p. 379.
[2] *Gamma Ray Energy Tables for Neutron Activation Analysis*, Filby, R. H., Davis, A. I., Shah, K. R., Wainscott, G. G., Haller, W. A., and Cassatt, W. A., Eds., Nuclear Radiation Center, Pullman, Washington, Report No. WSUNRC-97(2), 1970.