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Optimization of Firearm Residue Detection by Neutron Activation Analysis

The availability of high resolution Ge-Li detectors combined with automated data reduction enable refinements in the presently used technique of firearm discharge residue detection by adding ^{133}Ba and ^{124}Sb tracers as internal standards and by coprecipitation of Sb_2S_3 and BaSO_4 . This procedure reduces the manipulations of radioactive substances and increases the reliability of the results.

Neutron activation of Sb and Ba, present in the primers of most firearm ammunition, is a well established method for the detection of firearm residue. While there have been attempts to improve and simplify sampling techniques [1], the radiochemical procedure for separating Ba and Sb from interfering activities, notably ^{24}Na , their quantitative recovery has received only scant attention [2] since the inception of the neutron activation method [3,4].

Both Ba and Sb have relatively long lived gamma emitting isotopes; 7.2 year ^{133}Ba and 60 day ^{124}Sb which are not produced in significant amounts during the short irradiations used in the firearm residue analysis. The prominent photo peaks of 80.8 and 602.7 keV of ^{133}Ba and ^{124}Sb , respectively, can therefore be conveniently referenced with 165.8 and 564.0 keV neutron induced activities of 83 min ^{139}Ba and 2.7 day ^{122}Sb . The less than 2 keV full width half maximum (FWHM) resolution of our Ge-Li detector assures by a wide margin against any mutual peak interference; the 511 keV annihilation peak of ^{64}Cu and even 559.2 keV peak of ^{76}As which is often present in firearm discharge residue, are easily discernible. A reevaluation and modification of radiochemical and instrumental techniques yielded the following improvements:

1. Coprecipitation of Ba and Sb(5) reduces the manipulation of radioactive substances by eliminating one precipitation and filtration step. It also eliminates sample changing and shortens analysis time.
2. Addition of ^{133}Ba and ^{124}Sb tracers and manipulation of the data in terms of activity ratios $^{139}\text{Ba}/^{133}\text{Ba}$, $^{122}\text{Sb}/^{124}\text{Sb}$ eliminate, to a large extent, random errors thus increasing the precision several fold. The lack of uniform tracer activity in all samples at counting time may alert the analyst to abnormalities such as loss of sample, incomplete separations, etc.
3. Improved radiochemical procedures resulted in chemical yields consistently near 100 percent.
4. Computerized data handling improved the efficiency of data gathering and manipulation.

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5. Practical hints on chemical operations, especially on the quantitative handling of Sb, should be useful to the uninitiated in minimizing frustrations and in the saving of time.

This work, which did not involve actual firing of weapons, reestablishes the radiochemical and instrumental procedures only. A following phase is planned which will utilize the developed analytical technique to establish the degree of proficiency and reliability of various sampling techniques utilizing actual firings under controlled conditions. At this time a more involved statistical treatment and multivariate analysis will be attempted. We feel that the reevaluation is warranted by the recent improvements in instrumentation and data handling techniques and by the proposed improvements of the radiochemical procedures.

Experimental

In view of the scarcity of information on the basic chemistry involved in firearm discharge residue detection and the anticipation that more crime laboratories may become interested in this field, considerable effort was spent in establishing the adequacy and the quantitative nature of the chemical procedure including the analysis of the carrier solution. Next, the tracer yields of ^{124}Sb and ^{133}Ba were established; and, finally, the proposed technique was radioanalytically tested on synthetic samples—chemical standards. In all instances, sufficient replications were provided to establish statistical significance of the results.

Chemical Yields

The carrier solution was analyzed by precipitating separately Ba as the sulphate and Sb as the sulphide. Ba and Sb were coprecipitated typically from a 10 ml standard carrier solution as BaSO_4 and Sb_2S_3 by adding a mixture of aqueous solution of Na_2SO_4 and thioacetamide (TAA) in about 50 percent excess. The combined precipitate was then transferred by suction to a filter paper in a Buchner funnel. The chemical yield of Sb was determined by dissolving Sb_2S_3 off the filter paper (in a beaker) using 6 *N* HCl. The HCl treatment also disintegrates the filter paper so that BaSO_4 and the pulp can be separated from the solution by centrifuging with several 6 *N* HCl washings. Sb in the solution was titrated with 0.1 *N* KBrO_3 solution. The pulp and BaSO_4 are once more filtered as before, transferred to a crucible, ignited at 800°C for a few hours, then weighed after cooling. The bromometric titration utilizes the red-ox reaction $\text{KBrO}_3 + 3\text{SbCl}_3 + 9\text{HCl} = \text{KBr} + 3\text{HSbCl}_6 + 3\text{H}_2\text{O}$. A 0.1 percent methylorange solution was used as indicator, and As_2O_3 was used as a primary standard [6]. A word of caution should be interjected. Before titration of the dissolved Sb^{3+} , all traces of H_2S (hydrolysis product of TAA) have to be removed by evaporation to approximately half of the original volume; titrate hot using a magnetic stirrer. This sharpens and accelerates the otherwise sluggish color change (red to yellow).

While the handling of BaSO_4 is straightforward, precipitation and quantitative transfers of Sb_2S_3 can be complicated. Homogeneous (TAA) precipitation and the properties of Sb_2S_3 precipitate have been described [7,8]. However, this work has revealed additional problems in the recovery of Sb_2S_3 which warrants the following comments. (Actually the "antimony problem" is not new as illustrated by this quote from a well-known forensic radiochemist, "Many a radiochemist has been frustrated by the almost whimsical behavior of antimony . . ." [9].)

A major source of error in the chemistry of Sb_2S_3 is related to the limited stability of the precipitate in solution. The maximum stability region seems to be between 1 to 4 *N* HCl.

Higher acidity leads to partial dissolution while partial hydrolysis occurs at lower acidities. It is, therefore, of utmost importance to prepare the carrier in 2 – 3 *N* HCl and carefully avoid excessive dilution or concentration by evaporation (HCl-H₂O forms an azeotrope at approximately 6 *N* HCl).

An annoying property of the Sb₂S₃ precipitate is its tendency to “creep” which makes a quantitative recovery from glassware difficult and also becomes a source of radioactive contamination. A method which eliminates the problem consists of the following steps:

1. Coat the inside of the beakers used for precipitation with silicone. This eliminates the “creep” but creates a “stick.” Hydrophobic Sb₂S₃ has affinity to silicone (the same is true for plastic ware).
2. Treat the solution containing a portion, about half of a 50 ml beaker, with alcoholic KOH which restores clean glass surface.
3. Remove the KOH solution with a syringe without affecting the silicone coating of the upper half of the beaker.

A similar problem occurs when filtering the precipitate into a Buchner funnel. Here the circumvention of loss of Sb₂S₃ by “creeping” off the filter paper involves filtering into a filter “cup” instead of a flat filter paper. Use a “flat” filter (Whatman #41) with a larger diameter than the funnel (7 cm filter paper into a 4 cm funnel). Press the moistened filter paper into the funnel by a circular object (piece of glass tubing) of a slightly smaller diameter, 3.5 cm, thus forming a cup. Gradual filtration will yield a quantitative containment.

Another source of difficulty in handling Sb₂S₃ is the colloidal nature of the “red” Sb₂S₃—the species which forms initially on precipitation. Fortunately, when coprecipitating with crystalline BaSO₄, the phase change to the more stable crystalline “black” Sb₂S₃ takes 30–40 min (filter into a Gooch crucible for weighing) which then can be dried at 110°C for 20–30 min without decomposition or oxidation.

Finally, a note on the preparation of the carrier solution by dissolving Sb₂O₃ in concentrated HCl which is a slow process: contrary to the statements in literature [7,8], there appears to be no significant loss due to volatility of SbCl₃ as long as some acid is still present.

Tracer Yields

In order to observe the counting statistics of coprecipitated ¹²⁴Sb and ¹³³Ba tracer and the recovery yields in chemical operations, 5, 20, and 100 μl amounts of the tracer stock solution were added to 10 ml of the carrier solution; and the counting statistics of ¹³³Ba and ¹²⁴Sb were determined in the coprecipitate. With compatible activities counting efficiency of Ba was approximately three times higher than that of Sb which is understandable because the counting efficiency of the 80.8 keV photo peak of ¹³³Ba is approximately ten times higher than that of 602.7 keV of ¹²⁴Sb. On the other hand the abundance of the Ba energy is several times lower. In order to obtain similar counting rates, the disintegration rate of ¹²⁴Sb should be several times higher. Consideration also has to be given to the “age” of the 60 day ¹²⁴Sb so that the final adjustment is made by trial and error.

Irradiation of Trace and Chemical Standards

Three sets of chemical standards in quadruplicate were prepared by pipetting *A*: 20, *B*: 40 and *C*: 100 μl of standard solution containing in μg *A*: 0.04 Sb and 0.4 Ba, *B*: 0.08 Sb and 0.8 Ba, and *C*: 0.2 Sb and 2.0 Ba in 1.5 ml snap cap polyethylene vials (Olympic

Plastics). (Attempts to use graphite cups were unsuccessful because of excessive absorption.) In addition, a constant amount, 20 μl of tracer solution, was added to each vial in which the activities of ^{133}Ba and ^{124}Sb were of comparable magnitude as those expected of the induced ^{139}Ba and ^{122}Sb near the middle of the concentration range (*B* samples). An additional two vials contained 20 μl of tracer solution only in order to monitor the induced ^{139}Ba and ^{122}Sb to the inactive carrier in the tracer. Two empty vials were also included to monitor polyethylene background. The solutions were carefully evaporated to dryness without affecting the vials. After the irradiation, each of the vials was leached in 10 ml of the carrier solution for 30 min. The vials were rinsed (3 *N* HCl) and enough H_2O added to compensate for evaporation losses. The carrier, tracer, and induced activity were coprecipitated, filtered, washed, dried by suction, and transferred to plastic Petri dishes (Milipore). The Petri dishes were taped to $2\frac{1}{2} \times 3$ in. cards for insertion in a sample holder for constant geometry counting. The leached vials were enclosed in somewhat larger secondaries and also mounted on cards for counting. Since some of the activity, particularly Sb, tended to remain in the vial, both the precipitate and the vial had to be counted.

As the spectra were collected, utilizing a calibrated Ge-Li detector and a 2048 channel analyzer system, the data was transferred to magnetic tape which in turn was processed by an IBM 360/75 computer. The processing consisted of reduction of data to integrated counts per peak at zero time (end of irradiation) and identification of peaks by a computer resident program [10] and a library of thermal-neutron activable nuclides.

Of practical interest is the use of a set of automatic Eppendorff micropipettes (5, 20, 100 and 500 μl) with disposable plastic tips (Brinkman Instruments) which was found to be convenient, fast, and accurate for transfer of active solutions with a minimum of contamination. Also, automatic 10 ml macropipettes (Miscomatic Dispenser) were reliable time savers. Disposable plastic Petri dishes 48×8.5 mm. were convenient "secondaries" for counting activity on filter paper. To keep the contamination at a minimum, the rim of the Petri dishes should be taped. The snap-cap vials could be easily handled and identified when placed in 2 ml clear plastic minibeakers which in turn could be securely inserted into grid positions on a standard spectrophotometric cell holder.

The irradiations were carried out in a well thermalized section (isotope tray) of Argonne's CP-5 reactor. The samples (16 polyethylene vials per run) were packed in a standard polyethylene secondary (4 vials per layer in 4 layers) and irradiated in a flux of approximately 5×10^{12} n/cm²/s overnight. The samples were processed in a hot lab adjacent to the reactor, packaged, and transferred to another building for counting. The activities were such that 5×10^3 to 10^4 counts could be collected in a few minutes. It can be anticipated that for routine operations much shorter irradiations in the pneumatic "rabbit" facility with a substantially higher flux will be preferred.

While separating the bulk of the activity all of the standard radiation safety precautions should be observed by working in a well ventilated hood, constant monitoring by a second person, etc. Wearing pallbearer gloves as secondaries was found to be an effective way to avoid direct skin contamination in cases when occasional pinholes develop (on opening snap-caps of vials) in surgical gloves.

Reagents

Chemical Standards

A stock solution of chemical standards was prepared by dissolving $\text{Ba}(\text{NO}_3)_2$ and $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2} \text{H}_2\text{O}$ potassium antimonyl tartrate (anions essentially neutron non-

activable, ^{42}K does not materially interfere) in such amounts (3.80588 and 0.54856 g/l, respectively) that after dilution of one to ten, 5 μl of the resulting solution corresponds to 0.01 μg Sb and 0.1 μg Ba, while a 100 μl transfer corresponds to 0.2 μg and 2.0 μg Sb and Ba respectively. These aliquots of the barium and antimony standards cover the range of values encountered in firearm discharge tests. Everytime a new experiment series is performed 500 μl of the solution is diluted to 5 ml and is promptly micropipetted into vials in order to minimize the loss of standards by absorption on container walls.

Tracers

The original stock solutions 1 ml each was purchased from Amersham-Searle Company: 0.1 microcurie ^{133}Ba as BaCl_2 in 1 *N* HCl with 13 μg carrier, 1 microcurie ^{124}Sb as SbCl_3 in 5 *N* HCl with 200 μg carrier. The activities were adjusted by micropipetting aliquots and diluting to such a level that 20 μl of combined Ba-Sb tracer yielded comparable activity as those exhibited by irradiated chemical standards.

The "spiking" stock solution should be in the microcurie/ml range. One curie equals 3.7×10^{10} disintegrations per second. Unfortunately the carrier in Sb tracer solution contains enough ^{121}Sb to produce significant amounts of ^{122}Sb upon irradiation. Carrier in the ^{133}Ba solutions did not interfere. In order to avoid unnecessary corrections; it was decided to purchase isotopically pure ^{123}Sb (\$20 per 20 mg, Isotope Div., Oak Ridge National Laboratory). Irradiation for a few months in the reactor will produce ^{124}Sb tracer free from ^{122}Sb . This amounts to at least a half year's supply. Care should be taken periodically to compensate for the loss of Sb tracer activity, while the 7.2 year half-life of ^{133}Ba assures virtually constant activity.

Carrier Solution and Coprecipitation Agents

Five mg per ml of elemental Ba and Sb each, when used routinely in 10 ml amounts, generate sufficient precipitate for convenient handling and analysis. On a one liter basis typically 5.98 g analytical grade Sb_2O_3 is dissolved in some 250 ml concentrated HCl and diluted to one liter with a solution containing dissolved 7.59 g BaCl_2 and approximately 0.5 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and KCl as holdback carrier (normally it is advisable to prepare more than one liter which, once analyzed, can be used for a long period of time). The coprecipitation agent saturated in thioacetamide (approximately 12 percent) and containing 10 percent Na_2SO_4 acted also as holdback carrier for sodium. Dropwise addition of 15 drops ($\frac{3}{4}$ ml) is sufficient to coprecipitate carrier in 10 ml stock solution.

Results

Analysis and Chemical Yield of Carrier Solution

Table 1 contains typical analytical data of 10 ml amounts of carrier solution by separate precipitation and coprecipitation (chemical yield) plus titration of Sb using analytical and automatic (Miscomatic) pipettes. Results and standard deviation of triplicate de-

TABLE 1—Chemical yields.

	Pipette	Ba	Sb
Separate	Analytical	100.1 \pm 0.4	98.5 \pm 0.5
Determinations	Automatic	98.1 \pm 0.8	97.6 \pm 0.2
Coprecipitation	Automatic	98.6 \pm 0.7	94.9 \pm 0.9

terminations are expressed in percent theoretical (weighed-in) yields. The precision of analytical and automatic pipettes are comparable, the relatively low yield of Sb is probably due to a more extended chemical processing.

Tracer Yield

Table 2 shows average relative (normalized) counts per minute per microliter from a 10 ml coprecipitate of carrier solution containing 5, 20, and 100 μ l amounts of tracer stock solution. The actual counts were between 10^4 to 10^5 . The error indicated is the standard deviation in percent of total counts for a triplicate determination for each concentration range.

TABLE 2—Tracer and chemical yields.

Stock Solution, μ l	^{133}Ba		^{124}Sb	
	Tracer Yield, cpm	Chemical Yield, %	Tracer Yield, cpm	Chemical Yield, %
5	222 \pm 0.4	98.7 \pm 0.2	224 \pm 0.5	94.7 \pm 3.7
20	228 \pm 0.8	98.8 \pm 0.3	237 \pm 0.8	98.2 \pm 1.8
100	236 \pm 0.2	98.4 \pm 0.7	230 \pm 0.3	97.0 \pm 1.2

The chemical yield was determined and tabulated as described earlier. The relatively large error in the Sb titration is probably related to the small amount of 0.1 *N* KBrO_3 needed, 8.5 ml. While the possible trend and relatively large disagreement in tracer yields is somewhat puzzling, the results are still reasonable in terms of the intent of the investigation.

Table 3 summarizes the results of the irradiation and coprecipitation of chemical standards utilizing tracers as internal standards. Corrections were made for absorption on vials and the ^{122}Sb activity produced by tracer carrier. The columns corresponded to the activities (computer converted into absolute decompositions per minute) of the 20, 40 and 100 μ l amounts of chemical standard stock solutions each containing 20 μ l of tracer stock solution. The row below represents the standard deviation in percent of the quadruplicate determination. The ratios 122:124 and 139:133, the activity ratios of the corresponding

TABLE 3—Neutron induced and tracer activities.

Activities	Chemical Standard and Tracer Stock Solution in Microliters		
	20	40	100
^{122}Sb	1.0×10^6	1.9×10^6	3.5×10^6
Standard deviation, %	17	17	29
^{124}Sb	1.0×10^6	1.0×10^6	0.8×10^6
Standard deviation, %	13	22	25
122:124	1.0	1.9	3.9
Standard deviation, %	5	6	5
^{139}Ba	4.7×10^6	9.3×10^6	2.1×10^7
Standard deviation, %	6	8	12
^{133}Ba	1.6×10^7	1.4×10^7	1.3×10^7
Standard deviation, %	8	7	10
139:133	0.3	0.7	1.7
Standard deviation, %	10	7	2

nuclides with the respective standard deviation, which, especially for Sb, are considerably less than the individual standard deviations. Moreover, taking the highest ratio, 3.9 for Sb and 1.7 for Ba, as 100 we obtain 100, 43 and 23 for Sb and 100, 42 and 18 for Ba paralleling closely original concentrations. Significant activities present in polyethylene vials were: ^{24}Na , ^{38}Cl , ^{64}Cu , ^{82}Br and ^{56}Mn .

Detector and Analyser System

Detector

Coaxial 43.5 cm³ Ge-Li-Nuclear Diodes
 Efficiency 7.4%
 FWHM = 2.4 keV at 1.33 MeV
 Peak to Compton: 30 to 1

Associated Electronics

Power Supply—Ortec 401A-402A
 Preamplifier—Nuclear Diodes 110
 Bias Supply—Ortec 456
 Amplifier—Ortec 451

Analyser

2048 Channel ADC—Norther Scientific-615
 Interfaced with Magnetic Tape Drive—Kennedy 1400R

A more thorough report on detector-analyzer system which utilizes a Digital Equipment Corporation's PDP-12 computer for data acquisition and evaluation is forthcoming.

Conclusions

An investigation of the chemistry and radiochemistry involved in firearm discharge residue detection has been carried out. The usefulness of internal standards was demonstrated. The details and pitfalls were pointed out for the benefit of the novice worker planning to acquire Neutron Activation Analysis capability. We hope that this investigation will receive constructive criticism from the experienced workers in the field and hopefully serve as the beginning of a uniform radiochemical procedure for the detection of firearm residue.

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