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Firearm Residue Detection by Instrumental Neutron Activation Analysis

The neutron activation technique for firearm residue detection [1] is well known but not extensively applied. Additional work utilizing an optimized firearm residue detection technique by neutron activation analysis (NAA) [2] it made it clear that postirradiation radiochemical separations are the cause of several limitations which discourage a more general use of neutron activation analysis. The inherent time limitation due to 87-min half-life of ^{139}Ba necessitates fast manipulations of radioactive solutions, which in turn requires an experienced radiochemist. In addition, there is an ever-present danger of overexposure and contamination. Besides, typically only a dozen samples can be irradiated per batch, which makes the method quite expensive. The developed statistical treatment bivariate-normal analysis [3] is inconvenient for routine applications. With this in mind, a method was developed which: (1) eliminates postirradiation radiochemistry and thus maximizes time for analysis, (2) accommodates over 100 samples per irradiation capsule (rabbit); (3) does not require a collection of occupational hand blanks, and (4) utilizes a simplified statistical concept based on natural antimony (Sb) and barium (Ba) levels on hands for the interpretation of data [4].

Briefly, a cotton swab technique is employed and Sb and Ba are fixed on the cotton of the swab by moistening it with solution of the thioacetamide (TAA) and then with diluted sulfuric acid. The cotton of the swab is then stripped and soluble interfering materials, notably NaCl, are removed by leaching with $2N$ H_2SO_4 and methanol. The treated cotton is compacted into a small piece of ¼-in. polyethylene tubing and irradiated.

In order to place the present technique in proper perspective, a short review of sampling, analysis, and interpretation techniques of previous work on firearm residue detection by NAA may be appropriate.

The original work [1] and later investigation by high speed photography and auto-radiography [5] conclude that Ba from primer and Sb from both primer and bullet are deposited on the back of the firing hand as discrete particulate matter. The obvious problem for the detection of firearms residue on skin is the efficiency of collection, both from the standpoint of convenience and quantitation. After exploring a variety of methods, paraffin cast was suggested as the best [6], while another investigation suggests a complete hand rinse [7] as the most quantitative technique. Collodion lifts have been reported [8], and a

comparison between collodion lifts and filter paper swabs concludes [5] that both techniques are about equally efficient. Sampling by moistened cotton swab has been suggested [8-10] as a convenient technique.

While there has been considerable experimentation with sampling techniques, there have been few attempts to improve the analytical technique. The original separation technique [1] has undergone only minor changes [9,11].

There have been two attempts to optimize the radiochemical procedure and improve the accuracy by introducing Ba and Sb tracers [2, 12] and by reexploration of Sb radiochemistry [2]. A purely instrumental method has been reported [8] for Sb only, after allowing interfering activities to decay, including ^{139}Ba.

The bivariate-log-normal analysis on data collected by Guinn and co-workers appears to be the only comprehensive statistical treatment on firearm residue detection by NAA [3]. The results of firing tests were related to hand blanks collected from individuals of different occupational backgrounds. A somewhat more empirical interpretation of the same data is also reported [13]. Additional, smaller scale collections of hand blanks have been recently reported [14,15].

Experimental

Test Kits and Sampling

Considering the experience of previous workers and the overriding need for ease and convenience for crime scene sampling, there was little doubt that cotton swabbing is the preferred sampling technique. Test kits include a ¼-oz polyethylene squeeze bottle (Continental Glass Co.), containing dilute (1:20) HNO_3, and five snap-cap polyethylene vials, 1.5 cm in diameter and 5 cm long (Olimpic Plastics). The vials are marked RB, RP, LB, LP, and C, respectively, to distinguish right (R), left (L), back (B), palm (P), and control (C). Each vial contains a plastic stem swab. We found it useful to put an additional spare swab in the C vial. The kit also contains a pair of plastic gloves, two plastic bags, rubber bands, an identification slip, and a list of instructions. The items are contained in a tubular, screw-capped, cardboard container. The use of vials as opposed to bags [9] as containers for swabs was preferred because of the much smaller potential surface contamination of the former. Gloves are worn during the swabbing to avoid contamination. The plastic bags are for covering hands when immediate sampling is impractical. The swabbing is done by light strokes, slowly rotating the swab, beginning with the palmar section and proceeding to the index and thumb with particular attention being paid to the web portion. After sampling, the swabs are returned to their respective vials and submitted to the lab for processing. The moistening of the swabs is done at the scene, since premoistened cotton tends to disintegrate within a few weeks.

Chemical Processing

The preirradiation processing technique was developed via an intermediate step which involved the dissolution of the cotton of the swab (see section on Alternative Techniques).

In order to establish optimum procedures, tracer experiments were performed using 10.7-year ^{133}Ba and 60-day ^{124}Sb. Besides their convenient half-lives, their prominent photo peaks of 356 and 603 keV have detection efficiencies reasonably compatable with 166 and 564 keV photo peaks of neutron-induced ^{139}Ba and ^{122}Sb. The experiment showed that by using the mass action law, nearly 100% detention of $BaSO_4$ and Sb_2S_3 could be achieved at nanogram levels; that is, the use of a neutron insensitive, chemically similar carrier was not

even needed (see section on Alternative Techniques). It can be surmised that cotton fibers act as an ion exchange bed, absorbing the ionic species of Ba and Sb on active sites during the sampling and permanently fixing these ions as insoluble $BaSO_4$ and Sb_2S_3 during the chemical processing. All the chemical processing, which includes fixation of Ba and Sb and leaching of water solubles, is performed on the cotton of the swab. Therefore, it is important that the cotton be dried after each operation.

The first step in the processing is air drying the swab after removing it from the original vial and placing it tip up in another vial. Circular plastic trays with depressions (Curtin Chemical Co.) were found useful when handling a large amount of samples. Care should be taken to remove residual droplets of solution by absorbing them on the respective swabs and redrying. The next step is the deposition of one drop of saturated (approximately 10%) TAA solution on the cotton. After drying, a drop of $2N H_2SO_4$ is deposited on the cotton, which fixes Ba and releases H_2S to precipitate Sb. After drying again, the cotton is stripped from the plastic stem for the leaching process. The first leaching is carried out in $2N H_2SO_4$ containing a drop of TAA in the original sample vial. The purpose of this step is two-fold: to counter dissolution of the fixed $BaSO_4$ and Sb_2S_3 and to dissolve and diffuse out water solubles. This step should allow ample time (overnight) to achieve the exchange of Na^+, Cl^-, and Br^- ions on the cotton with H^+ and $SO_4^=$ ions of the solution. The next step is the removal of the aqueous solution from the cotton by absorbing on filter paper; the final leaching is in methanol. Finally, the cotton is stuffed into a $3/8$-in.-long piece of $1/4$-in. polyethylene tubing and dried.

Marking and Coding

The large number of samples which have to be accommodated in the irradiation capsule (rabbit) make careful marking and coding very important. Typically, some 130 samples fill the 3-cm-diameter and 7-cm-long irradiation capsules. Close packing is essential in order to avoid uncontrolled disordering due to rapid acceleration and deceleration in the pneumatic system. There are several categories of samples: (1) actual cases, (2) test firings, (3) hand blanks, (4) chemical standards, and (5) swab blanks (controls). Normally, all categories are included in an irraidiation batch and careful consideration has to be made as to the amount and relative location of each category. (Chemical standards from a stock solution can be conveniently and accurately deposited on swabs using automatic micropipets of 5, 10, and 20-μl capacity.) Vials are carefully marked throughout processing, the last marking being on the $1/4$-in. polyethylene tubing. In addition, each layer has its "floor map." Errors are also minimized by coding according to the sampling function; for example, RB (right-hand back) was recognized by the digit 1 while RP carried a 2: 01, 11, 21, etc and 02, 12, 22, etc. All the precautions were found to be very useful, especially during the brisk Ba count.

Irradiations

Our sample was irradiated in the rabbit facility of the CP-5 reactor at Argonne National Laboratory. The neutron flux is approximately 5×10^{13} $n/cm^2 \cdot s$. Optimum conditions were obtained by 40-min irradiation with immediate counting for Ba, and 5-h reirradiation and 2-day "cooling" before Sb analysis. The irradiation periods were sufficient to yield a few hundred counts per photo peak per minute, after one half-life for 10-ng Ba and 1-ng Sb level. ^{24}Na interference is minimal although ^{56}Mn in some instances (probably depending on the batch of cotton) can be bothersome in Ba count.

Analysis Procedure

The computerized analyzer, various peripherals available, and the manufacturer's (Digital Equipment Corp.—DEC) supplied software made the analysis both efficient and simple. It involved four stages: (1) collection of raw data and deposition on magnetic tape, (2) elimination of reagent and cotton background by channel by channel subtraction, (3) correction for Compton effect, and (4) net peak integration.

Of the various pulse height analysis programs supplied by DEC, the one named MSINGS proved to be the most convenient. It provides for two 1024-channel data areas in the computer 8K memory (maximum count of 4096 per channel) and for deposition on and recall from a magnetic tape. The visual display of all of the 1024-channel spectrum or any section of it during data collection is a valuable aid. After accumulation of the raw data, the spectra can be manipulated by recalling into memory. A convenient feature is the subtraction of a spectrum residing in Data Area 2 from that of Data Area 1. In this manner, cotton and reagent blanks on C (control) swabs can be subtracted from actual sample swabs. The net peak count was obtained by displaying and integrating the desired photo peak, typically five channels plus five adjacent channels, and subtraction of the compton background. All the operations are accompanied by printouts if desired. The responses were instantaneous and were initiated by teletype commands. The 1024-channel program (there is a 4096-channel version) was ample for firearm residue analysis. The energy range was such that the 1368 keV peak of ^{24}Na was included.

Detector and Analyzer System

Detector

   Nuclear diodes coaxial Ge-Li 45.3 cm^3
   Efficiency: 7.4%
   FWHM: 2.4 keV at 1.33 MeV
   Peak to Compton Ratio: 30 to 1
Associated Electronics
   Power Supply: Ortec 401A/402A
   Preamplifier: Nuclear Diodes 110
   Amplifier: Ortec 451
   Bias Supply: Ortec 451
Analyzer
   Packard 960/961 8K channel ADC
   Interfaced with PDP 12/40 computer via NNO1-A interface supplied by DEC

Alternative Techniques

Since it was recognized that postirradiation separation was a major drawback in firearm residue analysis, attempts were made to separate the potentially interfering elements, namely sodium (Na), chlorine (Cl), and bromine (Br), before irradiation. The method was based on the idea that due to their physical and chemical similarities, Bi_2S_3 could be used as a carrier for Sb_2S_3 and $SrSO_4$. Both natural bismuth (Bi) and ^{88}Sr are, for all practical purposes, thermal neutron insensitive. (Natural strontium could not be used due to massive ^{87}Sr interference.)

The water- and methyl-alcohol-soluble Na, Cl, and Br ions could be leached out of the precipitate by repeated washings. Briefly, the procedure was as follows. After sampling (swabbing), the cotton of the swab stripped from the stem, placed in a polyethylene vial,

and dissolved in a few drops of $3/4\ c$ H_2SO_4 (c H_2SO_4 chars). The solution was diluted, Sr and Bi carrier added, and the precipitation completed by addition of TAA. The precipitate was centrifuged, repeatedly washed, and finally dried. A drop of paraffin was deposited on top of the precipitate to prevent cross contamination and the empty portion of the polyethylene vial was cut off. Then, 50 such polyethylene vial bottoms could be loaded per irradiation batch. The interference levels were found to be tolerable and the method worked well. However, the present technique was found to be preferable.

Cursory attempts were made to develop alternate techniques to NAA, specifically by utilizing the conversion of Sb into volatile SbH_3 by reduction with $NaBH_4$. Both ultraviolet emission by excitation in a high voltage arc in a helium plasma, and flame atomic absorption, seemed to be useful techniques. The emission spectrometry appears to be particularly promising because of minimal expenditure for equipment. Additional work is necessary to improve the stability of the arc during the introduction of SbH_3. The atomic absorption work, using Perkin Elmer Model 303, yielded good sensitivity for Sb, but a careful optimization of all parameters and a sample volume of 0.5 ml were required to obtain satisfactory detection of Ba. It appears likely that the use of a more recent vintage of spectrometers will eliminate this problem.

Summary

Work leading to an improved technique for firearm discharge residue detection by neutron activation is described. The troublesome and time-consuming postirradiation chemistry has been eliminated; also, sample size has been minimized to accommodate some 130 samples per irradiation capsule. To put the method in a proper perspective, previous work has been referenced and discussed.

Acknowledgments

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