*J. T. Newton,* [1] *M.S.*

# Rapid Determination of Antimony, Barium, and Lead in Gunshot Residue Via Automated Atomic Absorption Spectrophotometry

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**ABSTRACT:** A rapid yet reliable method to detect the presence of antimony, barium, and lead in gunshot residue is employed to deal with the ever-increasing use of firearms in criminal cases. Since a reduction in analysis time and operator attention is realized, a more systematic approach can be used to deal with the significance of these three elements and their relation to gunshot residue. Residues are collected with cotton swabs and 5% nitric acid and are leached overnight in nitric acid. Enhanced reproducibility is also achieved when an automatic injector system is used instead of traditional manual pipet dispenser.

**KEYWORDS:** criminalistics, gunshot residues, spectroscopic analysis, antimony, barium, lead, flameless atomic absorption spectroscopy

In the past criminalists relied solely on color reactions when examining items for deposits of gunshot residues (GSR). These included the "dermal nitrate" test [*1*] and the Harrison and Gilroy tests for antimony, barium, and lead [*2*]. Such tests have merit when used in combination with powder patterns but lack specificity for determining the actual presence or absence of these elements.

The search for a more definite and reliable means of detecting GSR led to the introduction of neutron activation analysis (NAA) into this area [*3,4*]. This seemed to be the method of choice in the 1960s and early 1970s with interesting contributions from several workers [*5-16*]. The inability of NAA to detect lead prompted investigators to combine activation analysis with atomic absorption spectrophotometry (AAS) [*17,18*]. However, considering the cost of a nuclear reactor plus an atomic absorption spectrophotometer, the time-consuming radiochemical separation involved with NAA, and the overwhelming case load associated with the use of firearms, the most favorable method for a crime laboratory is atomic absorption.

Green and Suave [*19*] examined cotton swabs for antimony, barium, and lead in addition to copper using only absorption analysis, but the detection limits for antimony and barium in flame methods are undesirable because of the concentrations normally encountered in hand swabbings. Such inadequacies are eliminated with flameless atomic absorption spectrophotometry (FAAS). At first, furnace methods used tantalum liners [*20,21*] and

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[1]Chief chemist, Kentucky State Police Crime Lab, Frankfort, Ky.

strips [*22,23*], but Cone [*24*] has accurately and reliably detected all three elements using graphite tubes alone. Problems of high cost and sensitivity are avoided with furnace systems, but much time is involved dispensing each sample with a hand micropipetter into the furnace. Reproducibility is also a major factor in such a procedure because it depends on the analyst's technique and fatigue.

The method described in this paper concentrates on eliminating constant operator attention, and the irreproducibility associated with it, without sacrificing reliability and sensitivity. Thirty samples can be analyzed twice for one element in approximately 1 h while the operator is attending to other duties such as preparing laboratory reports, preparing samples, or examining and reflecting on previously collected data more thoroughly and completely.

## Experimental Methods

### *Equipment*

A Perkin-Elmer Model 5000 microcomputer-controlled atomic absorption spectrophotometer, equipped with a simultaneous double-beam background corrector, built-in automatic wavelength scanning and selection, and magnetic card reader, was used for all measurements. Hollow cathode lamps mounted on a six-lamp motorized turret were also used. Other equipment included the fully programmable HGA 500 graphite furnace and an AS-1 automatic sampling system. Measurements in concentration units were tabulated, averaged, and correlated on a PRS-10 printer-sequencer. Absorbance readings were registered on a Perkin-Elmer 156 recorder. Pyrolytically coated graphite tubes were used for both antimony and barium, while regular high density tubes were used in all lead analyses.

Standard solutions of antimony, barium, and lead were prepared from Fischer Scientific stock solutions (1000 ppm). Dilutions were made with 5% nitric acid (prepared from reagent-grade nitric acid and deionized water) and stored in polyethylene bottles.

Gunshot residues were removed from the palms and backs (web, forefinger, and thumb) of the hands with Johnson & Johnson plastic-stemmed cotton swabs and 5% nitric acid. Collected swabs were placed in separate polyethylene zip-lock bags until ready for use. Prior to analysis the cotton tips were snipped off and placed in 2-mL plastic conical beakers with 1 mL of 5% nitric acid. After the collected swabs sat overnight, each was shaken for approximately 30 s on a Fischer Scientific Vortex Genie Mixer and placed in individual preassigned slots on the AS-1 sampler carousel.

### *Atomization*

As with all graphite atomizers, operating conditions must be selected for each individual element. Table 1 lists the elements and the times and temperatures considered optimum in this investigation. Use is made of the optical sensor mounted on the atomizer chamber, prolonging tube life and increasing sensitivity. Over 200 shots per tube can be realized with antimony and lead, while the more refractive barium uses a tube every 100 to 150 shots, depending on tube manufacture. Argon is used in the atomizer chamber to maintain an inert atmosphere throughout the drying, ashing, and atomization cycles. No other gas is needed for cleaning, as confirmed by the absence of residual antimony, barium, and lead in later sequential blank firings. Flow rates are optimized throughout the three stages by using programmed gas-interrupt phases. All operating conditions including gas-interrupt phases were programmed onto a magnetic card and reintroduced into the furnace whenever necessary. Settings used on the spectrophotometer were obtained from Ref *25*.

TABLE 1—*Operating conditions for the HGA 500 graphite furnace.*

| | Antimony | | | Barium | | | Lead | | |
|---|---|---|---|---|---|---|---|---|---|
| Condition | Dry | Ash | Atomize | Dry | Ash | Atomize | Dry | Ash | Atomize |
| Temperature, °C | 120 | 600 | 2400 | 120 | 1100 | 2700 | 120 | 500 | 2000 |
| Ramp, s | 10 | 5 | 0 | 10 | 15 | 0 | 10 | 5 | 0 |
| Hold, s | 20 | 10 | 7 | 20 | 15 | 3 | 20 | 10 | 5 |
| Inert gas, mL/min | 200 | 200 | 50 | 300 | 300 | 150 | 200 | 200 | 150 |

## Results and Discussion

Before any conclusions can be reached relating the presence of antimony, barium, and lead to GSR, a normal search must be conducted of the hands of persons in various occupations who have not fired a weapon ("occupational handblanks"). Such a survey must be performed with the same collection procedure adopted for subsequent samples. Most occupational data compiled thus far have focused mainly on the back of the hand or the whole hand. However, a better overall picture can be observed by considering all four areas of the hand—left palm (LP), left back (LB), right palm (RP), and right back (RB)—and their relationships to each other in addition to absolute values. A few typical handblank values are listed in Table 2, with overall averages included in Table 3.

The detection of these three elements on normal hands is no novelty. In no way should the absolute amount of a relatively abundant element such as lead serve as a main criterion in determining that it is indeed from primer residue. At the same time, more emphasis should be attributed to such elements as antimony because of their environmental rarity.

It is well known that several variables are involved in the persistence of primer particles on the firing hand. Kilty [*15*] has researched this aspect in some detail. It is evident that minimal activity is conducive to retention, such as in suicide cases. Therefore, a most informative comparison would be of people in their normal daily activity to victims in confirmed suicides. Handblanks usually show the following relationships:

(1) larger concentrations of barium and lead on the palms of the hands than on the backs,
(2) approximately equal concentrations of barium and lead on the palms,
(3) approximately equal concentrations of barium and lead on the backs, and
(4) no significant amount of antimony.

Conversely, in suicides a significant increase of all three elements (except with .22-caliber weapons) is observed on at least one portion of the hand (Table 4). Relationships noted in results from normal hands are significantly altered in those from the hands of suicide victims. Also worthy of mention is the appearance of residues on the nonfiring hand in many suicide cases, possibly a result of bracing the weapon or of a last-minute reflex to ward off imminent danger.

Although not appearing as regularly as in suicides, residue deposits are evident in other cases involving the use of firearms. Table 5 gives a few results from tests of persons who have been involved in various criminal activities. Considerable difference is noted from handblank data. Contrary to suicides, other cases depend on such factors as time and activity, and the persistence of residues is not expected to be as pronounced as in suicides. Contacting other material, including rubbing the firing hand onto the nonfiring hand, causes transference from one surface to another, altering even further the original deposition.

Another point worthy of observation and consideration is that of known homicide victims. Hand swabs taken from these subjects often reveal considerable quantities of antimony, barium, and lead (Table 6), indicating a close-range firing, where the victim might extend

TABLE 2—*Occupational handblank data.*

| | Antimony, μg | | | | Barium, μg | | | | Lead, μg | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Occupation | LP | LB | RP | RB | LP | LB | RP | RB | LP | LB | RP | RB |
| Dentist | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.02 | 0.00 | 0.13 | 0.05 | 0.17 | 0.03 |
| Secretary | 0.00 | 0.00 | 0.00 | 0.00 | 0.10 | 0.04 | 0.14 | 0.07 | 0.14 | 0.09 | 0.25 | 0.06 |
| Credit clerk | 0.02 | 0.01 | 0.01 | 0.01 | 0.28 | 0.14 | 0.22 | 0.16 | 0.63 | 0.12 | 0.45 | 0.15 |
| Chemist | 0.01 | 0.00 | 0.01 | 0.00 | 0.11 | 0.05 | 0.11 | 0.03 | 0.18 | 0.08 | 0.17 | 0.04 |
| School teacher | 0.00 | 0.00 | 0.00 | 0.00 | 0.11 | 0.02 | 0.10 | 0.04 | 0.15 | 0.03 | 0.17 | 0.05 |
| Janitor | 0.02 | 0.01 | 0.01 | 0.01 | 0.17 | 0.09 | 0.24 | 0.08 | 0.50 | 0.24 | 0.48 | 0.22 |
| Unemployed | 0.00 | 0.00 | 0.00 | 0.00 | 0.17 | 0.03 | 0.25 | 0.13 | 0.11 | 0.03 | 0.15 | 0.03 |
| Teacher | 0.01 | 0.01 | 0.01 | 0.00 | 0.29 | 0.19 | 0.25 | 0.12 | 0.50 | 0.32 | 0.38 | 0.20 |
| Construction worker | 0.01 | 0.00 | 0.01 | 0.01 | 0.46 | 0.22 | 0.51 | 0.15 | 0.62 | 0.34 | 0.84 | 0.40 |
| Plumber | 0.00 | 0.00 | 0.00 | 0.00 | 0.46 | 0.21 | 0.55 | 0.16 | 0.25 | 0.09 | 0.15 | 0.03 |
| Automobile maintenance worker | 0.00 | 0.00 | 0.00 | 0.01 | 0.21 | 0.18 | 0.29 | 0.12 | 2.58 | 1.46 | 2.00 | 1.90 |
| Electrician | 0.00 | 0.01 | 0.00 | 0.00 | 0.15 | 0.10 | 0.26 | 0.06 | 1.18 | 0.36 | 0.66 | 0.22 |
| TV repairer | 0.00 | 0.00 | 0.00 | 0.00 | 0.16 | 0.11 | 0.27 | 0.11 | 0.94 | 0.30 | 1.24 | 0.54 |
| Mechanic | 0.01 | 0.01 | 0.00 | 0.00 | 0.88 | 0.50 | 0.88 | 0.48 | 9.07 | 4.75 | 10.4 | 6.91 |
| Factory | 0.00 | 0.00 | 0.01 | 0.01 | 0.36 | 0.20 | 0.26 | 0.19 | 0.74 | 0.38 | 0.56 | 0.31 |
| Iron worker | 0.01 | 0.02 | 0.01 | 0.01 | 0.33 | 0.20 | 0.28 | 0.19 | 1.26 | 0.84 | 1.38 | 0.80 |
| Housekeeper | 0.00 | 0.00 | 0.01 | 0.00 | 0.05 | 0.02 | 0.10 | 0.06 | 0.19 | 0.07 | 0.21 | 0.07 |
| Welder | 0.01 | 0.01 | 0.00 | 0.00 | 0.72 | 0.56 | 0.84 | 0.68 | 0.46 | 0.26 | 0.46 | 0.26 |
| Mechanic | 0.01 | 0.01 | 0.01 | 0.01 | 0.28 | 0.09 | 0.33 | 0.18 | 0.29 | 0.13 | 0.35 | 0.19 |
| Laborer | 0.01 | 0.00 | 0.01 | 0.00 | 0.12 | 0.03 | 0.08 | 0.06 | 0.27 | 0.07 | 0.26 | 0.15 |
| Oil distributor | 0.04 | 0.02 | 0.04 | 0.02 | 0.76 | 0.36 | 0.72 | 0.42 | 1.67 | 0.69 | 2.15 | 1.77 |

TABLE 3—*Summary of data collected from test firings and handblanks.*

| | | Average Antimony, μg | | | | Average Barium, μg | | | | Average Lead, μg | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | *n* | LP | LB | RP | RB | LP | LB | RP | RB | LP | LB | RP | RB |
| .357 | 15 | ... | ... | 0.04 | 0.03 | ... | ... | 0.15 | 0.17 | ... | ... | 1.25 | 1.10 |
| .38 | 94 | ... | ... | 0.03 | 0.05 | ... | ... | 0.25 | 0.39 | ... | ... | 1.41 | 1.03 |
| .32 | 24 | ... | ... | 0.10 | 0.10 | ... | ... | 0.60 | 0.76 | ... | ... | 1.62 | 1.08 |
| .25 | 22 | ... | ... | 0.09 | 0.14 | ... | ... | 0.67 | 0.86 | ... | ... | 1.16 | 0.68 |
| .22 | 76 | ... | ... | 0.02 | 0.01 | ... | ... | 0.18 | 0.17 | ... | ... | 1.26 | 0.77 |
| 9 mm | 5 | ... | ... | 0.02 | 0.15 | ... | ... | 0.27 | 1.82 | ... | ... | 0.89 | 1.39 |
| Shotguns | 45 | 0.02 | 0.01 | 0.03 | 0.01 | 0.17 | 0.09 | 0.22 | 0.16 | 0.82 | 0.46 | 0.92 | 0.53 |
| Rifles | 15 | 0.01 | 0.02 | 0.02 | 0.02 | 0.27 | 0.18 | 0.24 | 0.16 | 0.72 | 0.39 | 1.11 | 0.48 |
| Handblank | 73 | 0.01 | 0.01 | 0.01 | 0.01 | 0.18 | 0.10 | 0.20 | 0.11 | 0.78 | 0.32 | 0.74 | 0.42 |

the hands for protection or make a last-minute effort to grasp the weapon from his assailant. Evidence of this type, coupled with determinations of distance from powder patterns, could add valuable information about a particular confrontation. In several of these cases, as with some suicides, there is a rather large increase in the concentrations of antimony and lead on one or more particular areas of the hand while the change in the barium concentration is not as pronounced. This finding indicates that the antimony and lead originate not only in the primer but also in the projectile, although a complete record of bullet types (jacketed, unjacketed, copper-coated) was not kept.

TABLE 4—*Cases involving confirmed or highly suspected suicides.*

| | | Antimony, μg | | | | Barium, μg | | | | Lead, μg | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Case | Caliber | LP | LB | RP | RB | LP | LB | RP | RB | LP | LB | RP | RB |
| 1 | .22 | 0.01 | 0.00 | 0.00 | 0.00 | 0.15 | 0.27 | 0.05 | 0.02 | 1.46 | 0.62 | 0.10 | 0.18 |
| 2 | .38 | 0.02 | 0.03 | 0.07 | 0.19 | 0.18 | 0.14 | 0.54 | 0.74 | 0.37 | 0.67 | 1.03 | 3.67 |
| 3 | .38 | 0.09 | 0.09 | 0.01 | 0.03 | 0.78 | 0.48 | 0.08 | 0.26 | 0.75 | 1.15 | 0.07 | 0.33 |
| 4 | 20 gauge | 0.06 | 0.06 | 0.01 | 0.01 | 0.10 | 0.16 | 0.04 | 0.02 | 0.58 | 0.40 | 0.14 | 0.12 |
| 5 | .38 | 0.02 | 0.03 | 0.12 | 0.24 | 0.11 | 0.05 | 0.37 | 0.57 | 0.46 | 0.38 | 1.00 | 1.74 |
| 6 | .38 | 0.12 | 0.00 | 0.00 | 0.00 | 0.74 | 0.04 | 0.16 | 0.02 | 2.23 | 0.09 | 0.15 | 0.11 |
| 7 | .38 | 0.01 | 0.01 | 0.01 | 0.16 | 0.05 | 0.06 | 0.10 | 1.16 | 0.15 | 0.16 | 0.37 | 1.07 |
| 8 | .25 | 0.02 | 0.06 | 0.00 | 0.01 | 0.18 | 0.46 | 0.07 | 0.03 | 0.44 | 0.38 | 0.22 | 0.24 |
| 9 | .22 | 0.01 | 0.01 | 0.01 | 0.01 | 0.59 | 0.08 | 0.11 | 0.11 | 0.94 | 0.32 | 0.48 | 0.48 |
| 10 | .22 | 0.01 | 0.03 | 0.00 | 0.00 | 0.62 | 1.15 | 0.18 | 0.28 | 1.50 | 7.50 | 0.46 | 0.62 |
| 11 | .38 | 0.01 | 0.01 | 0.01 | 0.06 | 0.14 | 0.05 | 0.22 | 0.33 | 0.16 | 0.14 | 0.42 | 0.90 |
| 12 | 12 gauge | 0.01 | 0.02 | 0.22 | 0.31 | 0.17 | 0.19 | 0.64 | 0.53 | 1.70 | 1.34 | 2.44 | 1.74 |
| 13 | .32 | 0.24 | 0.02 | 0.04 | 0.03 | 0.70 | 0.29 | 0.61 | 0.32 | 5.55 | 0.53 | 0.93 | 0.35 |
| 14 | .38 | 0.00 | 0.00 | 0.02 | 0.03 | 0.00 | 0.00 | 0.09 | 0.09 | 0.10 | 0.04 | 0.50 | 0.68 |
| 15 | .38 | 0.00 | 0.00 | 0.01 | 0.03 | 0.03 | 0.02 | 0.16 | 0.29 | 0.29 | 0.15 | 0.65 | 0.89 |
| 16 | .38 | 0.09 | 0.03 | 0.01 | 0.02 | 0.78 | 0.33 | 0.14 | 0.16 | 1.78 | 1.10 | 0.40 | 0.34 |
| 17 | .41 | 0.39 | 0.70 | 0.03 | 0.06 | 1.78 | 3.00 | 0.55 | 0.53 | 15.0 | 31.2 | 1.18 | 2.74 |
| 18 | 20 gauge | 0.02 | 0.01 | 0.10 | 0.02 | 0.11 | 0.03 | 0.45 | 0.13 | 0.79 | 0.33 | 2.25 | 1.07 |
| 19 | .38 | 0.01 | 0.02 | 0.06 | 0.02 | 0.06 | 0.02 | 0.99 | 0.30 | 0.30 | 0.31 | 0.59 | 0.17 |
| 20 | .38 | 0.08 | 0.03 | 0.03 | 0.03 | 1.72 | 0.84 | 0.55 | 0.56 | 2.69 | 0.87 | 0.89 | 0.41 |

TABLE 5—*Cases involving nonsuicidal incidents.*

| | | Antimony, μg | | | | Barium, μg | | | | Lead, μg | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Case | Offense | LP | LB | RP | RB | LP | LB | RP | RB | LP | LB | RP | RB |
| 1 | assault | 0.02 | 0.02 | 0.05 | 0.03 | 0.26 | 0.14 | 0.62 | 0.46 | 0.19 | 0.33 | 0.47 | 0.57 |
| 2 | murder | 0.00 | 0.00 | 0.07 | 0.01 | 0.35 | 0.27 | 0.70 | 0.14 | 0.11 | 0.03 | 0.85 | 0.43 |
| 3 | murder | 0.32 | 0.06 | 0.21 | 0.17 | 1.50 | 0.51 | 1.35 | 1.48 | 5.50 | 0.74 | 3.10 | 2.35 |
| 4 | murder | 0.02 | 0.00 | 0.01 | 0.14 | 0.90 | 0.33 | 0.61 | 1.90 | 3.20 | 1.40 | 2.75 | 8.30 |
| 5 | murder | 0.02 | 0.02 | 0.12 | 0.01 | 0.41 | 0.25 | 0.76 | 0.24 | 1.14 | 0.74 | 1.94 | 0.48 |
| 6 | murder | 0.21 | 0.26 | 0.01 | 0.00 | 1.35 | 2.48 | 0.24 | 0.08 | 1.46 | 1.72 | 0.24 | 0.12 |
| 7 | assault | 0.07 | 0.04 | 0.03 | 0.05 | 0.75 | 0.81 | 0.54 | 1.15 | 9.15 | 2.72 | 2.58 | 6.30 |
| 8 | assault | 0.05 | 0.06 | 0.19 | 0.04 | 0.49 | 0.69 | 0.64 | 0.58 | 1.76 | 5.55 | 5.10 | 2.00 |
| 9 | wanton endangerment | 0.11 | 0.01 | 0.01 | 0.01 | 0.62 | 0.23 | 0.14 | 0.11 | 3.68 | 2.66 | 1.26 | 0.95 |
| 10 | murder | 0.00 | 0.00 | 0.00 | 0.18 | 0.10 | 0.09 | 0.15 | 0.32 | 0.39 | 0.23 | 0.67 | 6.21 |

## *Gun Tests*

Since this method was initiated in our lab, several weapons have been test-fired and the hands of the shooter subsequently tested for GSR. These firearms, representing approximately only a one-year period, were forwarded to our labs by various police agencies as having been used in the commission of a crime. Hands were thoroughly washed and dried immediately before and swabbed immediately after each test fire. Representative results from various handguns are given in Tables 7 to 10 and summarized, with handblanks, in Table 3.

Weapons individually listed (except .22 caliber) are those that show considerable amounts

TABLE 6—*Results of swabbings from homicide victims.*

| | | Antimony, μg | | | | Barium, μg | | | | Lead, μg | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Case | Caliber | LP | LB | RP | RB | LP | LB | RP | RB | LP | LB | RP | RB |
| 1 | .22 | 0.00 | 0.01 | 0.04 | 0.00 | 0.36 | 0.38 | 0.84 | 0.38 | 0.90 | 1.02 | 3.32 | 0.68 |
| 2 | .22 | 0.00 | 0.00 | 0.00 | 0.00 | 0.52 | 0.14 | 0.10 | 0.10 | 2.07 | 0.41 | 0.19 | 0.09 |
| 3 | .38 | 0.04 | 0.02 | 0.18 | 0.07 | 0.54 | 0.06 | 0.68 | 0.34 | 0.08 | 0.02 | 1.70 | 0.94 |
| 4 | .45 | 0.74 | 0.00 | 0.00 | 0.00 | 5.69 | 0.57 | 0.83 | 0.31 | 4.88 | 0.45 | 0.59 | 0.35 |
| 5 | .38 | 0.02 | 0.01 | 0.08 | 0.05 | 0.55 | 0.29 | 0.53 | 0.65 | 0.61 | 0.19 | 3.81 | 6.31 |
| 6 | .22 | 0.00 | 0.11 | 0.00 | 0.00 | 0.11 | 0.10 | 0.29 | 0.15 | 0.60 | 1.70 | 0.66 | 0.48 |
| 7 | 12 gauge | 0.06 | 0.02 | 0.09 | 0.07 | 0.18 | 0.20 | 0.16 | 0.25 | 3.22 | 2.20 | 7.35 | 7.35 |
| 8 | .38 | 0.00 | 0.00 | 0.07 | 0.01 | 0.35 | 0.17 | 0.70 | 0.14 | 0.11 | 0.03 | 0.85 | 0.43 |
| 9 | 30-30 | 0.01 | 0.09 | 0.04 | 0.00 | 0.10 | 0.53 | 0.27 | 0.38 | 1.18 | 14.55 | 0.60 | 2.94 |
| 10 | .357 | 0.01 | 0.01 | 0.31 | 0.02 | 0.52 | 0.25 | 2.18 | 0.31 | 0.35 | 0.19 | 2.43 | 0.23 |

TABLE 7—*Test firings of various .38-caliber revolvers (one shot).*

| | | Antimony, μg | | Barium, μg | | Lead, μg | |
|---|---|---|---|---|---|---|---|
| Type | Ammunition | RP | RB | RP | RB | RP | RB |
| Rossi | Remington-Peters | 0.31 | 0.07 | 0.92 | 0.52 | 3.09 | 1.15 |
| Smith & Wesson | Remington-Peters | 0.05 | 0.22 | 0.84 | 1.38 | 0.43 | 0.87 |
| Rossi | Remington-Peters | 0.04 | 0.10 | 0.36 | 0.61 | 2.50 | 2.16 |
| Colt | Remington-Peters | 0.02 | 0.13 | 0.22 | 1.16 | 0.59 | 0.39 |
| Smith & Wesson | Winchester-Western | 0.05 | 0.12 | 0.24 | 0.64 | 0.44 | 0.50 |
| Taurus | Winchester-Western | 0.04 | 0.21 | 0.15 | 0.52 | 1.00 | 0.54 |
| Arminius | Smith & Wesson | 0.10 | 0.10 | 0.54 | 0.42 | 0.88 | 0.72 |
| Charter Arms | Winchester-Western | 0.03 | 0.13 | 0.38 | 0.78 | 1.17 | 1.35 |
| Liberty Arms | Remington-Peters | 0.11 | 0.51 | 0.45 | 0.51 | 2.28 | 2.36 |
| Smith & Wesson | Remington-United Metallic Cartridge | 0.01 | 0.09 | 0.16 | 0.78 | 1.10 | 0.42 |
| Smith & Wesson | Remington-Peters | 0.04 | 0.07 | 0.86 | 1.56 | 1.05 | 0.39 |
| Charter Arms | Reload | 0.04 | 0.07 | 0.51 | 1.13 | 2.69 | 4.91 |

TABLE 8—*Test firings with various .32-caliber weapons (one shot).*

| | | Antimony, μg | | Barium, μg | | Lead, μg | |
|---|---|---|---|---|---|---|---|
| Type | Ammunition | RP | RB | RP | RB | RP | RB |
| Rossi | Winchester-Western | 0.02 | 0.05 | 0.20 | 0.24 | 0.23 | 0.83 |
| Clerke 1st | Remington-Peters | 0.30 | 0.20 | 1.06 | 1.08 | 2.81 | 2.41 |
| Iver Johnson | Remington-Peters | 0.04 | 0.13 | 0.60 | 2.08 | 0.84 | 0.42 |
| Harrington & Richardson | Winchester-Western | 0.04 | 0.20 | 1.00 | 0.86 | 0.72 | 2.46 |
| Harrington & Richardson | Remington-Peters | 0.10 | 0.19 | 0.49 | 1.73 | 2.46 | 1.77 |
| Smith & Wesson | Remington-Peters | 0.05 | 0.07 | 0.42 | 0.72 | 0.53 | 0.57 |
| Smith & Wesson | Remington-Peters | 0.03 | 0.05 | 0.63 | 0.68 | 1.32 | 1.08 |
| Omega | Remington-Peters | 0.24 | 0.22 | 1.89 | 2.10 | 4.76 | 4.53 |
| Smith & Wesson | Winchester-Western | 0.32 | 0.06 | 0.66 | 0.12 | 2.41 | 0.45 |
| Harrington & Richardson | Winchester-Western | 0.03 | 0.08 | 0.20 | 0.40 | 0.51 | 0.53 |
| Harrington & Richardson | Remington-Peters | 0.07 | 0.08 | 0.62 | 0.72 | 0.99 | 0.49 |
| Harrington & Richardson | Remington-Peters | 0.23 | 0.05 | 0.58 | 0.46 | 2.58 | 0.80 |

TABLE 9—*Test firings of various .25-caliber automatic weapons (one shot).*

| | | Antimony, μg | | Barium, μg | | Lead, μg | |
|---|---|---|---|---|---|---|---|
| Type | Ammunition | RP | RB | RP | RB | RP | RB |
| Galesi | Winchester-Western | 0.05 | 0.24 | 0.30 | 1.30 | 0.48 | 0.42 |
| Excam | Remington-Peters | 0.15 | 0.15 | 2.13 | 1.11 | 0.29 | 0.18 |
| Excam | Winchester-Western | 0.26 | 0.35 | 0.97 | 1.27 | 0.46 | 0.42 |
| Galesi | Remington-Peters | 0.09 | 0.09 | 0.50 | 0.58 | 0.59 | 0.29 |
| Titan | Winchester-Western | 0.11 | 0.74 | 0.27 | 1.45 | 0.88 | 0.94 |
| Bauer | Remington-Peters | 0.15 | 0.14 | 1.35 | 1.91 | 1.25 | 0.67 |
| Raven Arms | Winchester-Western | 0.03 | 0.10 | 0.58 | 1.11 | 2.64 | 1.16 |
| Raven Arms | Remington-Peters | 0.08 | 0.11 | 0.61 | 0.65 | 1.64 | 0.94 |
| Raven Arms | Remington-Peters | 0.02 | 0.12 | 0.46 | 2.93 | 0.44 | 0.56 |
| Titan | Federal | 0.28 | 0.17 | 2.44 | 1.22 | 1.82 | 1.22 |
| Colt | Remington-Peters | 0.18 | 0.09 | 0.44 | 0.26 | 2.34 | 0.75 |
| Raven Arms | Remington-Peters | 0.03 | 0.23 | 0.47 | 1.72 | 0.21 | 0.33 |

TABLE 10—*Test firings of various .22-caliber weapons (one shot).*

| | | Antimony, μg | | Barium, μg | | Lead, μg | |
|---|---|---|---|---|---|---|---|
| Type | Ammunition | RP | RB | RP | RB | RP | RB |
| Rohm Gesellschaft 14 | Winchester-Western | 0.01 | 0.01 | 0.05 | 0.07 | 0.57 | 0.55 |
| Llama | Winchester-Western | 0.01 | 0.01 | 0.30 | 0.18 | 1.60 | 0.96 |
| Astra | Remington-Peters | 0.03 | 0.03 | 0.32 | 0.32 | 1.74 | 1.20 |
| Rohm Gesellschaft 10 | Remington-Peters | 0.01 | 0.01 | 0.04 | 0.02 | 0.76 | 0.50 |
| Iver Johnson | Remington-Peters | 0.13 | 0.07 | 0.54 | 0.20 | 3.32 | 1.52 |
| EIG Derringer | Remington-Peters | 0.03 | 0.02 | 0.04 | 0.02 | 1.06 | 0.53 |
| Rohm Gesellschaft 23 | Federal | 0.03 | 0.04 | 0.42 | 0.48 | 1.13 | 1.95 |
| Rohm Gesellschaft 23 | Remington-Peters | 0.00 | 0.01 | 0.03 | 0.07 | 1.44 | 0.50 |
| Rohm Gesellschaft 23 | Cascade Cartridge Inc. | 0.02 | 0.01 | 0.51 | 0.07 | 1.30 | 0.48 |
| Sports King Auto | Federal | 0.01 | 0.04 | 0.08 | 0.47 | 0.69 | 1.37 |
| H. Schmidt | Federal | 0.07 | 0.03 | 0.68 | 0.23 | 2.63 | 1.39 |
| Taurus | Remington-Peters | 0.00 | 0.00 | 0.06 | 0.04 | 0.76 | 0.50 |

of residue. However, such amounts are not always the case. Some weapons do not emit because of their tightness, and this must be considered when control firings are compared to actual case shootings. The revolver involved in Case 14 in Table 4 failed to emit appreciable antimony or barium when test-fired. Failure of a weapon to deposit may explain a lack of residues from individual hand swabbings. It is also clear that residues are not necessarily more concentrated on the back of the hand. It is possible, especially with lead, to find more on the palms from mere manipulation of the gun and this must also be considered.

Careful deliberation must be undertaken with .22-caliber weapons because, on the average, the results from these guns strongly resemble those from handblanks. The absence of the relatively rare antimony in rim-fire ammunition, as noted in Table 11, places a burden on the analyst in decisions involving these firearms. However, .22-caliber ammunition does not necessarily preclude detecting antimony; note the results from the Iver

Johnson revolver given in Table 10. The antimony is possibly from residual traces from a previous firing with a primer containing antimony and barium. Results from rifles shown in Table 3 are not surprising since all were .22 caliber.

### *Ratio and Reproducibility Studies*

Computing ratios of the three elements to one another has been attempted with limited success, as observed by others [*16,17,26*]. Calculating elemental proportions from test firings reveals promising yet variable results, as shown in Table 12. However, ratios become less valuable when they are compared to handblanks and actual case situations. When handblanks are examined, barium/lead is usually the only possible ratio because of the absence of antimony on most of these hand swabs. If we also consider the absolute variability of these elements on "normal" hands of different people, ratios become even less meaningful. As pointed out by Guinn [*13*], occupational levels of one group may show high lead content but low barium, and vice versa on others. When this information is coupled with the numerous variables involved in the actual discharging of a weapon (such as bullet, firing chamber, individual cartridge manufacture, overall conditions of gun, and amount of back pressure developed), it is concluded that ratios have little value in gunshot residue determinations.

Besides eliminating constant operator attention, automatic sampling systems offer reproducibility not achieved by conventional hand micropipetters (Figs. 1 to 3). Standard deviations of 0.5 and 0.7% were realized with 0.10 and 0.05 ppm antimony, respectively, with the automatic injection, while 3 and 2% standard deviations were observed from the

TABLE 11—*Swabbings from .22-caliber cartridge cases.*

| Ammunition | Antimony | Barium | Lead |
|---|---|---|---|
| Winchester-Western Short | ND[a] | X | X |
| Winchester-Western Long Range | ND | X | X |
| Winchester-Western Magnum | ND | X | X |
| Cascade Cartridge Inc. Short | ND | X | X |
| Cascade Cartridge Inc. Long Range | ND | X | X |
| Cascade Cartridge Inc. Magnum | ND | X | X |
| Remington-Peters Short | ND | ND | X |
| Remington-Peters Long Range | ND | ND | X |
| Federal Short | X | X | X |
| Federal Long Range | X | X | X |

[a] Not detected.

TABLE 12—*Elemental proportions as determined from test firings (mean plus or minus standard deviation).*

| Weapon/Hand Location | Antimony/Barium | Barium/Lead | Antimony/Lead |
|---|---|---|---|
| .38/RP | 0.15 ± 0.10 | 0.47 ± 0.51 | 0.06 ± 0.04 |
| .38/RB | 0.23 ± 0.26 | 1.25 ± 1.19 | 0.17 ± 0.12 |
| .32/RP | 0.18 ± 0.14 | 0.56 ± 0.34 | 0.07 ± 0.04 |
| .32/RB | 0.17 ± 0.12 | 1.04 ± 1.30 | 0.11 ± 0.07 |
| .25/RP | 0.17 ± 0.13 | 0.17 ± 0.18 | 1.47 ± 1.97 |
| .25/RB | 0.19 ± 0.13 | 0.14 ± 0.31 | 2.68 ± 1.96 |

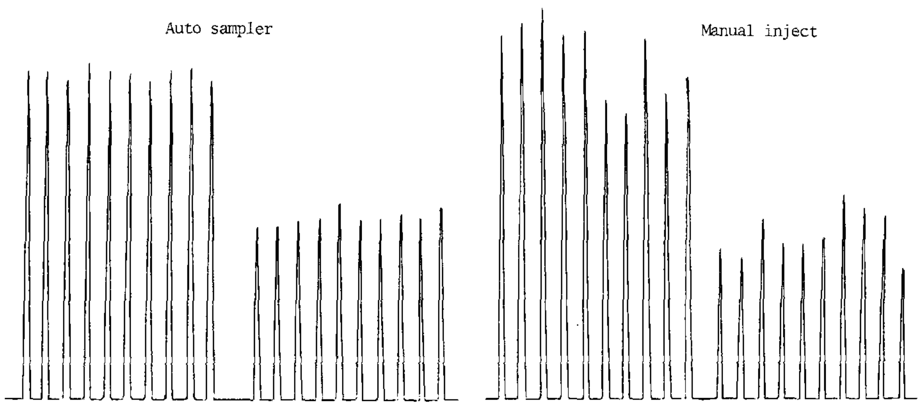


FIG. 1—*Comparison of automatic sampling and manual injection with 0.05 and 0.10 ppm antimony standard solutions.*

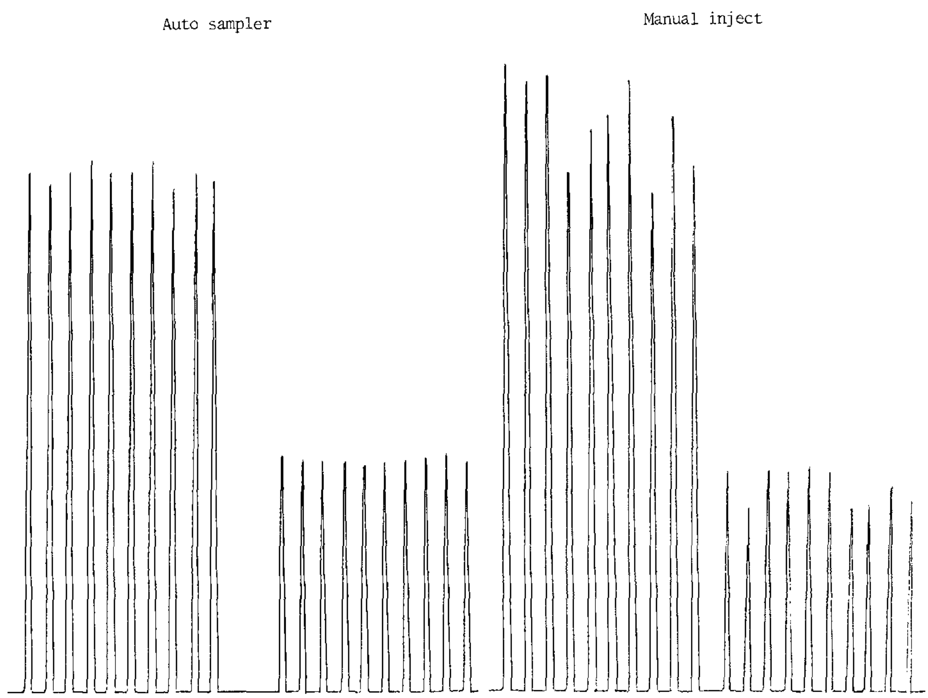


FIG. 2—*Comparison of automatic sampling and manual injection with 0.10 and 0.25 ppm barium standard solutions.*

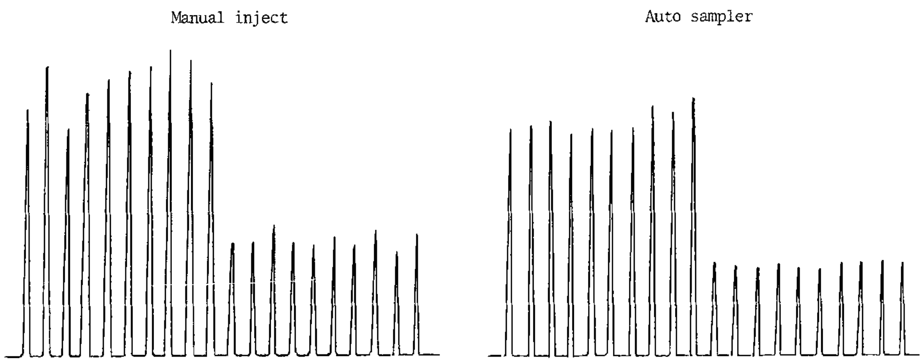


FIG. 3—*Comparison of manual injection and automatic sampling with 0.10 and 0.25 ppm lead standard solutions.*

same solutions with manual injection. With 0.10 and 0.25 ppm barium standard solutions, 0.4 and 0.9% standard deviations for automatic injection were obtained, as compared with 2 and 4% standard deviations for manual injection. Comparable results were obtained with standard solutions of lead. Of course, manual injections vary from day to day and time to time within a day, depending on the disposition of the analyst. Automatic injections do not depend on that factor.

## Summary

A method for rapid detection of antimony, barium, and lead in GSR has been developed to deal with the tremendous case load involving firearms. Comparison of hand swabbings from different areas of "normal" hands and firing hands offers a better indication of GSR. Given the influx of samples, such comparisons are possible only with automation, with consequent elimination of constant operator attention. Reproducibility is also enhanced as compared to hand pipetting by such systems. Not all weapons emit primer residue, but on the average, hands swabbed after the discharge of a firearm show amounts of some elements that are greater than occupational levels.

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Address requests for reprints or additional information to
John T. Newton
Kentucky State Police Crime Lab
1250 Louisville Rd.
Frankfort, Ky. 40601