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## A Rapid Microtechnique for the Detection of Trace Metals from Gunshot Residues

The detection of primer and gunshot residues is important to the criminalist. Several techniques to detect trace materials have been proposed as providing definitive proof that primer or gunshot residue is present [1-8]. While the dermal nitrate-nitrite test has been shown to yield misleading information [1], tests based on the detection of one or more of the metals lead, barium, antimony, and copper appear to be much more reliable [8].

These metals have been found in small amounts as gunshot residues by a variety of methods which either require very specialized equipment, such as neutron activation analysis or atomic absorption spectrophotometry [3], or are very indiscriminate, such as spot tests with sodium rhodizonate [4]. Another analytical method, involving the use of the Weisz ring oven [9] to localize, concentrate, separate, and identify the four metals of interest from each other and from possible interfering ions and other extraneous matter, is described below.

### Apparatus

The Weisz ring oven consists of a cylindrical block of aluminum, 35 mm wide by 55 mm high (1.38 by 2.15 in.), with a 22-mm (0.86-in.) diameter hole. A heating element is installed in the block, and a temperature of 105 to 110°C (221 to 230°F) is maintained with a variable transformer. The application of an aqueous solvent to the center of a piece of filter paper on the block with a capillary pipet results in a concentrically spreading circle of liquid. As the solvent spreads, it reaches the edge of the hole and is vaporized, leaving any dissolved components concentrated in a "ring zone." The commercial ring oven (National Appliance Co., Portland, Ore.) employed in this study had a small light bulb to locate the center of the filter paper accurately for sample placement and a guide tube for placement of the capillary washing pipet.

Since the area of the ring is smaller than the spot of the original test solution spot, any eluted component is effectively concentrated three to ten times. The ring formed has a circumference of about 70 mm (2.7 in.), which can be divided into sectors. Spot reactions for various ions can then be made on these aliquot portions of the ring. Since only aliquot portions of the test ring are used for color reactions, identification limits of the spot tests may be decreased if one has an ion concentration that approaches the lower limits of the spot test. This problem can be circumvented by using either less selective, but more sensitive, spot tests or by applying multiple samples to the filter paper.

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Two capillary pipets are used. One is a long, conically tapering capillary of about 0.1-mm (0.004-in.) inner diameter, which, refilled several times, serves as the "washing pipet." The other is similar but much shorter, having a capacity of 1.5  $\mu$ l. This pipet can be filled completely by merely touching it to the surface of the sample solution. Thus, very reproducible amounts of sample can be delivered to the same spot on the filter paper. If more than three drops are to be used, the spot should be allowed to dry to prevent spreading of the initial sample zone.

Throughout the tests gaseous reagents were employed where possible to prevent spreading and diluting the rings produced. A hydrogen sulfide ( $H_2S$ ) generator is also needed. Weisz [9, p. 11] describes several that function as a source of  $H_2S$  gas which can be drawn through the filter paper. The  $H_2S$  generator used in this study was constructed from a 125-ml filter flask, 60-ml separatory funnel, and a two-piece, 25-mm Kontes Chromaflex<sup>®</sup> chromatography column. Solid sodium sulfide is placed in the filter flask. The  $H_2S$  is generated by adding small amounts of concentrated hydrogen chloride (HCl) from the separatory funnel attached to the vacuum outlet of the filter flask. The stopcock portion of the chromatography column is attached to the filter flask with a rubber stopper. The sample is placed between the two sections of the chromatography column. To insure reaction of the sample with  $H_2S$ , the top of the chromatography column is attached to an aspirator and a partial vacuum is applied to the system.

Since one or a set of ions may be selectively washed away from a precipitated one or set of ions which remain in the center, a separation and identification scheme may be developed. Any number of separations can be effected by punching out the center disk, placing it on another filter paper, and washing with another solvent to produce another ring. Thus the analyst can work with even the most complicated separation scheme. Whatman 42 filter paper was used throughout this study, but if reagents that destroy normal filter paper are employed, glass fiber filter paper may be substituted as the support media. Weisz [9, p. 40] describes a separation scheme for 14 metal ions contained in a single drop; the scheme can be extended for up to 35 metals. Quantitative analysis may even be possible with a set of standard rings developed with stable, color-producing reagents.

### Materials and Methods

For sensitivity and familiarization studies, the initial separation scheme was patterned after Weisz [9, p. 27] and is given in Fig. 1. Known mixtures of nine metal ions, lead, antimony, nickel, manganese, tin, iron, chromium, barium, and copper, were prepared by diluting atomic absorption standard 1000 ppm solutions with deionized water. Table 1

TABLE 1—Analysis of synthetic mixture by the ring oven.

Element	Test Reagent	Color	Sensitivity by Ring oven, total $\mu$ g in ring
Pb	sodium rhodizonate	blue, red	0.05
Sb	rhodamine B	purple	0.15
Ni	dimethylglyoxime	red	0.05
Mn	$AgNO_3$	brown-black	0.05
Sn	morin	green fluorescence	0.05
Fe	potassium hexacyanoferrate	blue	0.05
Cr	benzidine	blue	0.05
Ba	sodium rhodizonate	red	0.15
Cu	benzoinoxime	yellow-green	0.05
	catalysis reaction	...	0.001

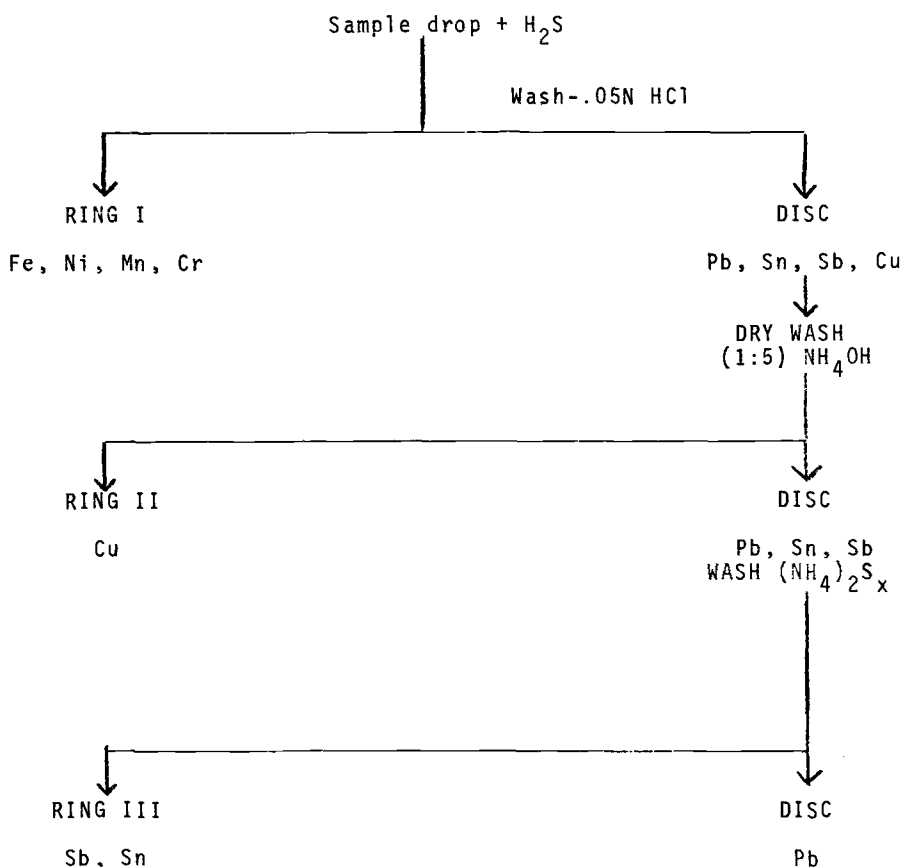


FIG. 1—Separation scheme for test solutions.

summarizes the results. Analysis time was approximately 90 min. The sensitivity of this technique appears high enough to detect levels of lead, barium, and antimony previously reported [8].

A Smith and Wesson .38 Special revolver with a 4-in. (101.6-mm) barrel was used for all test firings. The revolver was in good condition with a 0.1-mm gap between each chamber and the barrel. Lead Winchester and Remington 158 grain, .38 Special bullets and Luballoy® Western 158 grain, .38 Special bullets were used as ammunition.

Two types of gunshot residues were collected. The first type was from cardboard targets placed 6 in. (152.4 mm) from the muzzle of the revolver. Surface scrapings were taken from the bullet hole and 20 mm (0.8 in.) from the bullet hole. The second residue type was collected from cardboard tunnels placed around the revolver. These tunnels were usually torn by escaping gases at the firing chamber-barrel gap.

The grayish cardboard scrapings were placed in a spot-plate well and treated with one or two drops of 1:1 HCl. The paper was pulverized to aid dissolution; when the paper turned white, dissolution was considered to be complete.

The initial familiarization and test scheme was found to be unsatisfactory, and a modified scheme for the separation and identification of the four metal ions of interest is given in Fig. 2.

A sample spot of 1.5 or 3.0  $\mu\text{l}$  of the solution to be tested is placed on the filter paper, dried, moistened with one drop of absolute ethanol, and treated with hydrogen

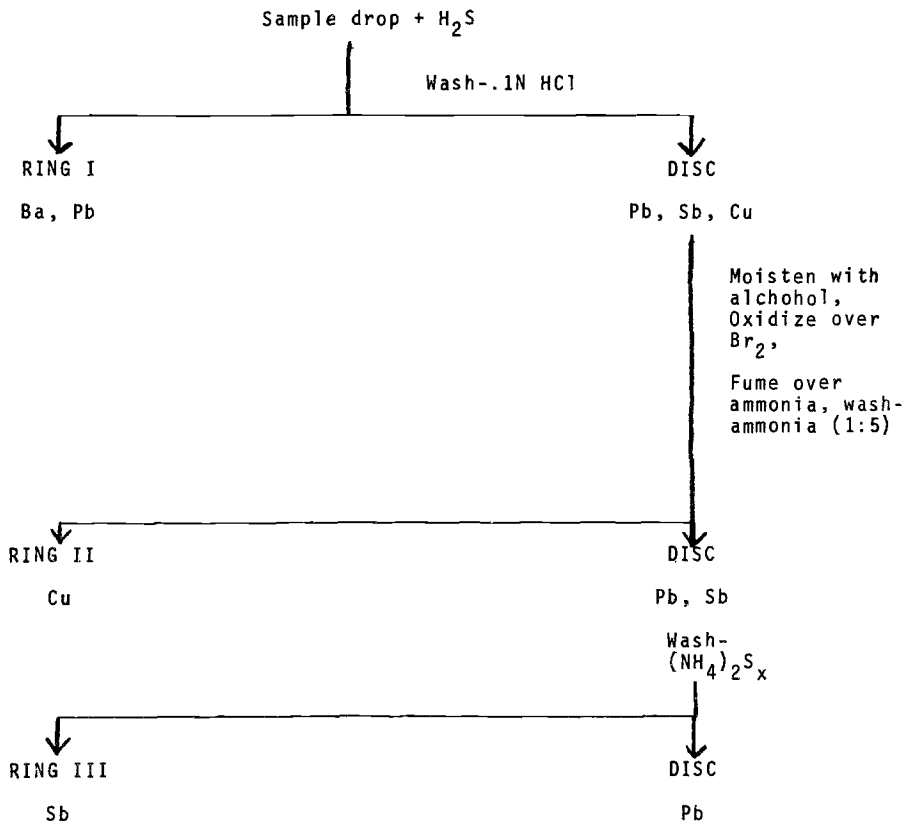


FIG. 2—Separation scheme for firearms residues.

sulfide in the gas generator. The first ring is produced with 0.1N HCl as wash solvent. Ring 1 contains barium and lead. With two pieces of freshly cut, concentric glass tubing, the middle of the paper is punched out (approximately 12-mm or 0.5-in. diameter) and placed in a holder described by Weisz [9, p. 14]. All manipulations of the disk are done either in the glass holder or with Teflon®-tipped forceps. The disk (D1) is fumed over bromine, then over ammonia, and dried over a spot plate; D1 is then centered on another filter paper, placed on the ring oven, and washed with dilute ammonia. Ring 2 now contains copper as the ammine complex. The disk is placed on a third filter paper and washed with yellow ammonium sulfide (concentrated NH<sub>4</sub>OH saturated with gaseous H<sub>2</sub>S). Ring 3 now contains antimony and lead remains in D1.

Ring 2 is analyzed for copper by a catalytic test rather than benzoinoxime, which produces a light green line not always visible at low concentrations. Copper catalyzes the reduction of iron by thiosulfate and the test is sensitive for amounts as small as 10<sup>-9</sup> g of copper. A sector of Ring 2 is dissected and placed on a spot plate. One drop of ferric thiocyanate solution (1.5 g FeCl<sub>3</sub>·6H<sub>2</sub>O + a few drops concentrated HCl + 2 KSCN + 100 ml H<sub>2</sub>O) is added, and after a few seconds two drops of 0.1N sodium thiosulfate are added. Copper is detected by a faster fading of the red solution compared with a blank test run on the filter paper. Feigl [10] has discussed the interesting set of reactions occurring in this test.

Antimony is detected with rhodamine B on a dissected sector of Ring 3 placed on a spot plate. One to two drops of 1:1 HCl are added, followed by one drop of 5%

potassium iodide (KI), then a few crystals of sodium sulfite. Mixing of the small solution is accomplished by blowing through a Pasteur pipet. One drop of 0.5% rhodamine B is then added and the solution mixed again. A distinct blue-violet precipitate appears when antimony is present. The color obtained should be compared to a paper blank, which usually is orange. The antimony complex must be extracted with two drops of benzene. The blue-violet color produced when antimony is present will selectively appear in the benzene layer [9, p. 30], while rhodamine B complexes of other metals are insoluble.

The disk D1 can be spotted with aqueous sodium rhodizonate for the detection of lead, indicated by a blue color when fumed over concentrated HCl. However, it was found that the disk gave erratic results. Lead is also found in Ring 1, with barium. Incomplete precipitation is thought to be responsible, but a topochemical effect may also be present. Autoxidation and fine dispersion are believed responsible for the solubility of lead sulfide in dilute HCl, which normally does not dissolve the compact sulfide. Coprecipitation with barium may also be responsible [11].

Therefore, the lead test was modified to be performed on Ring 1. A part of the ring is spotted with saturated sodium rhodizonate and fumed over glacial acetic acid. A red line is attributable to barium, the lead being masked as the acetate. If much barium is present, another sector is spotted with sodium sulfate. The sector is then spotted with saturated sodium rhodizonate and fumed over concentrated HCl. A blue line of lead complex is observed, as any barium sulfate present does not appear to interfere in any of the known test samples. Care must be taken not to dilute the lines by using too much reagent because the rings will not then be visible.

## Results and Discussion

Results obtained for several different types of ammunition fired from the same gun are summarized in Table 2. Each sample was the result of one test firing, and 1.5  $\mu$ l of

TABLE 2—Results of side chamber and target analysis by the ring oven.

Ammunition	Side Chamber				Target <sup>a</sup>			
	Ba	Cu	Sb	Pb	Ba	Cu	Sb	Pb
Winchester lead	++	++	++	++	++	++	++	+++
Remington lead	++	++	++	++	+	++	++	+++
Western Luballoy®	++	++	+++	++	++	++	++	+++

+ = Slight positive, blank

++ = Normal positive

+++ = Strongly positive

<sup>a</sup>Hole and 20 mm from hole.

solution was used. We did not observe gross differences in the amounts of metals found at the edge of the hole and 20 mm from the hole. The unexpected result (side chamber) obtained with Luballoy® ammunition, that is, larger amounts of antimony found rather than copper, was reproducible and might be a result of the relatively crude methods of quantitation. The results reported are not quantitative because this study was undertaken to develop a rapid screening method for the metal ions of interest. Significant variations in the absolute amounts of metals present have been reported by others [6-8]. Since only 1.5  $\mu$ l of approximately 60 or 120  $\mu$ l total for the target or side chamber samples and 1000  $\mu$ l total for handswab sample was used, quantitation by other more precise methods is possible and while recommended, requires additional study.

An analysis of hand residue was attempted next. Swabbing techniques similar to ones already described were used [8]. A small piece of filter paper was wrapped over the top of a Pasteur pipet and moistened with 0.1N HCl. The residue and much dirt were concentrated in a small ring around the ridge of the pipet; the rest of the filter paper was used for handling the swab. The paper was dried and the circular section of contact was cut out and placed in a micro test tube. Five drops of concentrated HCl and five drops of deionized water were added. The paper was then digested in a water bath until a brown solution remained. This solution, after centrifuging, was used to spot the paper for ring oven analysis. Two drops, 3.0  $\mu$ l, of this test solution were sufficient, but volumes up to 12.0  $\mu$ l made the tests even easier.

The detection of primer residues on hands was tested by two experiments. The shooter's hands were washed with tap water prior to discharging the .38 Special revolver described earlier. Both hands of the shooter were swabbed after one shot and after two shots. Lead Winchester ammunition was used in both cases.

Swabbings of both hands were taken in a room different from the one used to discharge the revolver. The shooter's hands were also swabbed after washing with laboratory tap water. The swabbings were divided into three groups: the palm, the entire fingers and thumb, and the back of the hand from knuckles to wrist. The results are summarized in Table 3. In all cases positive results are reported when the sample gave a test greater than the reagent blank. Division into more areas was not considered necessary, and it was indeed found that the heaviest residues are found on the back of the hand and the fingers, with the palm positive to a lesser degree. This localization of residues has been previously discussed [4].

The blank hand in both experiments showed no barium or lead. Slight positives were obtained for copper. A similar positive copper test was obtained when a coin, a metal-tipped pen, or a doorknob were handled. Slight positives for antimony were also observed. Both the ammonium sulfide reagent after storage in glass containers and tap water gave a positive antimony test of the same magnitude as the test of the fingers of the hand that had been washed but had not fired.

The ring oven shows much potential in forensic applications. Skill of the operator depends only on the extent to which the ring oven would be used. The ring oven can serve as a quick screening device for gunshot residues on hands or other objects. Additional work is needed to test the effects of different guns, ammunition, and environmental contaminants on the significance of results obtained by the ring oven.

### Summary

The most important facts and advantages of this method are as follows.

1. A simple separation and identification scheme for metals considered characteristic of gunshot residues was developed.
2. The apparatus used is inexpensive, simple, extremely versatile, and has moderate sensitivity.
3. Blanks of background ions present do not interfere with the test, but warrant consideration.
4. Few reagents are needed, and the results are preservable.

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TABLE 3—Analysis of hand swabs by the ring oven.

Element	Clean Hands						Hands Before 1 Test Shot						Hands After 1 Test Shot						Hands After 2 Tests Shots					
	Right			Left			Right			Left			Right			Left			Right <sup>a</sup>			Left		
	F	P	B	F	P	B	F	P	B	F	P	B	F	P	B	F	P	B	F	P	B	F	P	B
Ba	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cu	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sb	+	+	+	+	-	-	+	-	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

F = Fingers  
 P = Palm  
 B = Back

- = Negative  
 + = Slight Positive, blank  
 + + = Normal Positive  
 + + + = Strongly Positive

<sup>a</sup>Shooting hand.

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