# TECHNICAL NOTE

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# An Update on the Use of the Sodium Rhodizonate Test for the Detection of Lead Originating from Firearm Discharges

**REFERENCE:** Bartsch MR, Kobus HJ, Wainwright KP. An update on the use of the sodium rhodizonate test for the detection of lead originating from firearm discharges. J Forensic Sci 1996;41(6): 1046–1051.

**ABSTRACT:** We have made a comprehensive investigation of the chemistry associated with the Sodium Rhodizonate Test for particulate lead deposited on surfaces as a consequence of a firearm discharge. This has been directed at addressing some of the problems that have hitherto compromised the value of this test to forensic science. In particular, we have found that aqueous solutions of sodium rhodizonate are considerably more stable if stored below pH 3. The rhodizonate dianion is then diprotonated, forming rhodizonic acid, and the half-life of the solution increases from about one hour to about ten hours. By ensuring that the area to be examined is pretreated with tartrate buffer so that its pH is adjusted to 2.8 prior to treatment with rhodizonic acid, the formation of a nondiagnostic purple complex, instead of the desired scarlet complex, is avoided. Whereas the scarlet complex changes to a blue-violet complex, upon secondary treatment with 5% HCl, which is diagnostic of the presence of lead, the purple complex decolorises completely under these conditions and thus its formation represents wastage of lead from within the test area and is associated with the fading problem that has previously plagued the test. The fading of the blue-violet complex can be eliminated by removing excess HCl, by means of a hair drier once the color has fully developed.

**KEYWORDS:** forensic science, criminalistics, gunshot residue, sodium rhodizonate, lead

The Sodium Rhodizonate Test has been described and advocated in forensic chemistry literature (1,2) as a convenient field test that can be used to verify the presence or absence of lead deposits, particularly where the lead deposit may indicate the occurrence of a firearm discharge at the scene of a crime. The distribution of the lead deposit on a surface can be mapped by visual observation of the characteristic blue-violet coloration, preceded by a scarlet coloration that develops at the site of a lead, or lead containing particle when a series of reagents, which includes sodium rhodizonate, is sprayed onto the surface. By comparison of the lead distribution with a set of reference distribution patterns, some knowledge of the maximum muzzle to surface distance can be acquired (3).

Application of the test is not without its difficulties, however, and a recent article on the subject (1) has warned of two of them: The inherent instability of sodium rhodizonate, both in the solid state and in solution, and the tendency of the blue-violet coloration to fade "rapidly and unpredictably." Of these, the latter is the more serious as it means that the test, in its present form, cannot be relied upon to produce a positive result that can be displayed in its original form in a court of law. The first difficulty could be the cause of a false negative result, although if a successful trial test has first been carried out on a surface deliberately treated with lead, this should not occur.

The purpose of this article is to discuss the chemical origin of these problems and to present a revised procedure for the test that eliminates them. It should be noted, however, that as the detailed chemical structure of both the blue-violet compound formed from lead, and its scarlet colored precursor, remain unknown at this time, a full understanding of the chemical mechanism of the test is not yet possible. When synthesized in the laboratory, both compounds form as fine powders that are almost totally insoluble in solvents that do not decompose them. This has made it impossible to grow crystals of a sufficient size for single crystal X-ray diffraction studies, which otherwise could have led to a knowledge of their structures. Work is underway in our laboratories to deduce these structures from a combination of neutron and X-ray powder diffraction patterns, but this may take some considerable time to complete, if indeed, it can be done at all. Attempts have been made in this work to deduce the structures of the complexes from solid state infrared and NMR spectroscopic data and from UV/visible spectra, but they only serve to show that the compounds contain lead and rhodizonate or tetrahydroxyquinone (see below) without indicating the detailed structural arrangement of these entities, the atoms through which they coordinate, or the tautomeric form in which the ligands exist.

## Materials and Methods

### *In Vitro Syntheses of the Colored Lead Complexes Formed in the Test*

The following syntheses were carried out using sodium rhodizonate that was received from Aldrich immediately before the commencement of these experiments. It should be noted that sodium rhodizonate is not indefinitely stable in the solid state. Although

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Received for publication 23 Feb. 1996; accepted for publication 11 April 1996.

we do not have detailed information on its shelf-life, we did find that a 20-year-old sample of sodium rhodizonate from BDH was 50% decomposed (noted by the intensity of its visible absorption band at 482 nm using the literature value (4) of 3.2 by $10^4$ $M^{-1}$ $cm^{-1}$ for the extinction coefficient).

*The Purple Lead-THQ Complex*—An aqueous solution of lead nitrate (308 mg, 0.93 mmol in 100 mL of water) was brought to boil. This solution was combined with a solution containing sodium rhodizonate (100 mg, 0.46 mmol in 50 mL of water). The resulting purple precipitate was filtered off, washed separately with water and ethanol, and then dried under vacuum. Yield: 0.21 g. Percentage recovery of lead: 71.4%. (Found: C, 10.6; H, 0.2; N, 0.4; O, 22.5; Pb, 64.9%, broadly consistent with $Pb_2(THQH_{-3})NO_3$ which requires C, 11.2; H, 0.2; N, 2.2; O, 22.3; Pb, 64.2%). $^{13}C$ NMR (solid state) δ 190.2 (s), 177.5 (s), 172.4 (s), 162.5 (s) 98.3 (m), 84.8 (w), 78.1 (w), 64.1 (w). Infrared spectrum: (KBr disk) 3456 $cm^{-1}$ (s), 1594 (s), 1531 (m), 1385 (s), 1308 (m), 1079 (w), 1057 (w), and 772 (w). UV/Visible spectrum: $\lambda_{max}$ (0.5% HCl, the compound slowly decomposes in this medium, thus extinction coefficients could not be measured) 204 nm (s), 308 (m), 380 (sh), and 590 (w).

*The Scarlet Lead-Rhodizonate Complex*—A rhodizonic acid solution was prepared from sodium rhodizonate (100 mg, 0.47 mmol) and the pH 2.8 tartrate buffer solution (50 mL) prepared from tartaric acid (0.75 g, 5.0 mmol), and sodium hydrogen tartrate monohydrate (0.95 g, 5.0 mmol). The solution was added into a lead nitrate solution (232 mg, 0.7 mmol, in 100 mL of water) and the resulting scarlet complex was collected by filtration, washed separately with water and ethanol, and dried under vacuum. The complex was found to be stable indefinitely in the solid state. Yield: 0.23 g. Percentage recovery of lead: 89.4%. (Found: C, 13.5; H, 1.1; O, 29.5; Pb, 54.2%, broadly consistent with $Pb_3(C_6O_6)_2(OH)_2 \cdot 6H_2O$ which requires C, 13.1; H, 1.1; O, 29.2; Pb, 56.6%. $^{13}C$ NMR (solid state) δ 190.5 (w), 184.7 (m), 179.0 (s), 172.6 (w), 74.8(s). Infrared spectrum: (KBr disc) 3449 $cm^{-1}$ (s), 1669 (m), 1598 (s), 1534 (m) 1449 (s), 1420 (s), 1306 (m), 1264 (w), 1215 (w), 1133 (w), 1062 (w), 769 (w), and 677 (w). Visible spectrum: $\lambda_{max}$ (DMF, the compound slowly decomposes in this solvent thus extinction coefficient could not be measured) 582 nm.

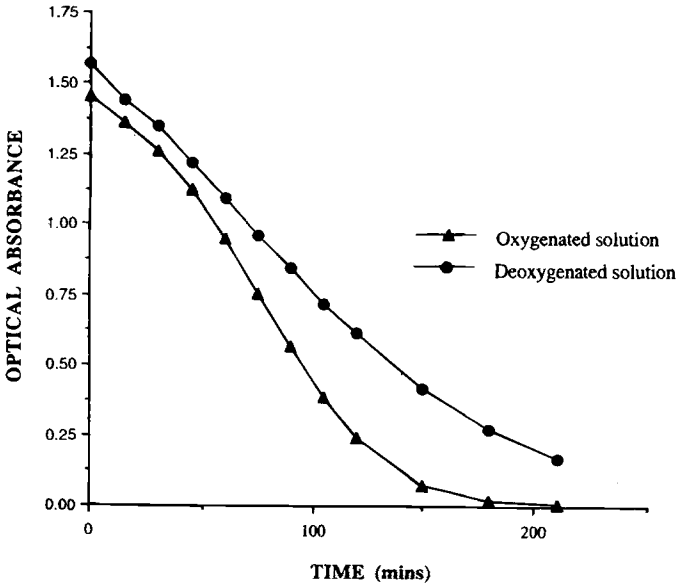



FIG. 1—*Showing the rate of decomposition of oxygenated and deoxygenated aqueous solutions of 4.65 by $10^{-5}$ M sodium rhodizonate. The absorbance at 482 nm (ε = 3.2 by $10^4$ $M^{-1}$ $cm^{-1}$) was monitored.*

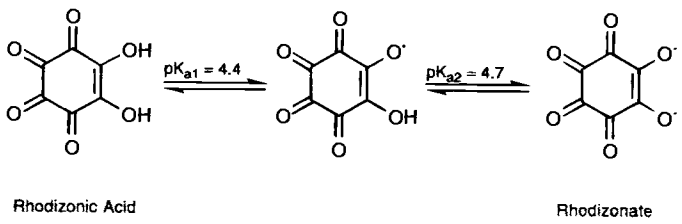



FIG. 2—*Acid base equilibria for rhodizonic acid. $pK_a$ values are taken from reference 7.*

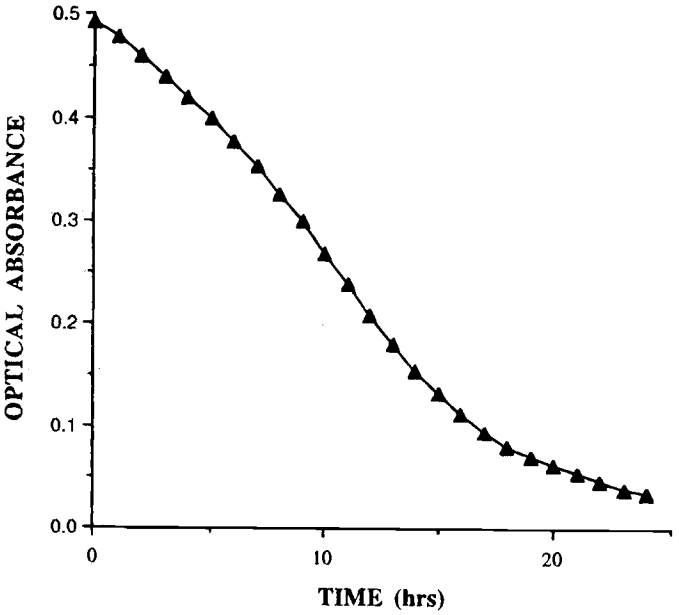



FIG. 3—*Showing the rate of decomposition of oxygenated 4.65 by $10^{-5}$ M rhodizonic acid in a pH 2.8 tartrate buffer solution. The absorbance at 320 nm (ε = 1.04 by $10^4$ $M^{-1}$ $cm^{-1}$) was monitored.*

*The Blue-Violet Lead-Rhodizonate Complex*—This was synthesized by taking an arbitrary amount of the scarlet complex and suspending it in a stirred 5% HCl solution (prepared from 5 mL of conc. aqueous HCl in 100 mL of water). The resulting blue-violet complex was recovered, washed separately with water and ethanol, and dried under vacuum. The complex was found to be stable indefinitely in the solid state. The yield was dependent on the stirring time. Anal. Found: C, 9.6; H, 0.6; Cl, 10.6; O, 17.9; Pb, 62.0, broadly consistent with $Pb_2(C_6O_6)Cl_2 \cdot 2H_2O$ which requires C, 10.4; H, 0.6; Cl, 10.3; O, 18.6; Pb, 60.1%. $^{13}C$ NMR (solid state) δ 190.5 (w), 179.2 (s). Infrared spectrum: (KBr disk) 3469 $cm^{-1}$ (s), 1673 (w), 1597 (m), 1526 (m), 1444 (s), 1403 (s), 1308 (w), 1061 (w), and 769 (w). UV/Visible spectrum: $\lambda_{max}$ (5% HCl, the compound slowly decomposes in this medium thus extinction coefficients could not be measured) 242 nm (s), 318 (m), and 608 (m).

*Formation of the Complexes on Paper from a Gunshot Residue*

A series of 0.22 in. calibre discharges was made through pieces of cloth from various ranges extending from 0 to 150 cm. The

residue adhering to the cloth was in each case transferred onto a filter paper using the Bashinski method as described by Dillon (1). The filter paper was then sprayed with an aqueous solution of pH 2.8 tartaric acid/monosodium tartrate buffer followed by saturated aqueous sodium rhodizonate solution (0.4 g/100 mL) or treated in one spraying with sodium rhodizonate that had been dissolved directly in the buffer solution until saturation point was reached (0.4 g/100 mL). In either method, the scarlet coloration appears instantaneously as a response to the presence of lead containing material, and is indefinitely stable. Before proceeding to the next stage, the filter paper was dried by a combination of blotting against a clean filter paper and treatment with a hair drier. The sample was then lightly sprayed with a 5% aqueous HCl solution until the blue-violet color of the formerly scarlet material had reached its maximum intensity. The filter paper was then quickly dried, again through a combination of blotting and use of a hair drier. By doing this, the blue-violet color was preserved indefinitely. It should be noted, however, that unless this final drying is accomplished quickly and thoroughly, fading of the blue-violet color will occur.

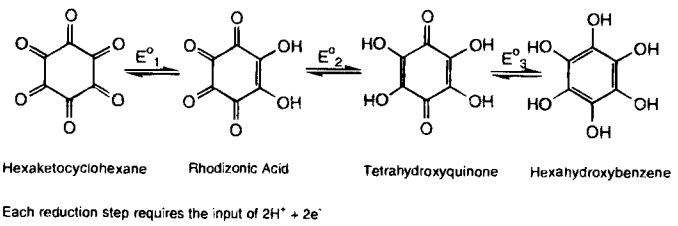



FIG. 4—*Redox equilibria in which rhodizonic acid can participate in a protic medium. Reduction proceeds from left to right.*

## Results and Discussion

### *Stability of Sodium Rhodizonate/Rhodizonic Acid*

As noted above, solid sodium rhodizonate, the form in which rhodizonic acid is normally supplied, slowly decomposes. However, this appears to be sufficiently slow, (having a half-life which is best measured in years) that it does not represent a serious problem, especially if samples are refrigerated and not exposed to light [the rate of the oxidative decomposition of rhodizonate is known to be enhanced both thermally and photochemically (5)]. In aqueous solution, however, the decomposition problem can be a more serious one, as the decay curves shown in Fig. 1 illustrate. Although not strictly decaying according to first order kinetics, the half-life of an oxygenated solution at its natural pH, as indicated by the time taken for its optical absorbance to reduce to one-half of its initial value, can be seen from its curve to be about 80 min, increasing to 105 min if the solution is prepared in the absence of oxygen. As the rate of decomposition has been shown to diminish with diminishing pH, (5), and because the Sodium Rhodizonate Test is carried out at pH 2.8, rather than at the naturally basic pH of a sodium rhodizonate solution (1,2), it occurred to us that a better way to handle solutions of this reagent would be to dissolve sodium rhodizonate directly in the tartrate buffer which is traditionally used (1) to achieve pH 2.8 at the test site. When this is done, the rhodizonate dianion becomes fully protonated and loses its orange color in accordance with the protonation scheme shown in Fig. 2. The resulting solution of rhodizonic acid has a UV absorption maximum at 320 nm ($\varepsilon$ = 1.04 by $10^4$ $M^{-1}$ $cm^{-1}$) consistent with literature data (4). By monitoring the disappearance of this absorption with time, the decay curve for rhodizonic acid shown as Fig. 3 was generated. This indicates an approximate half-life for

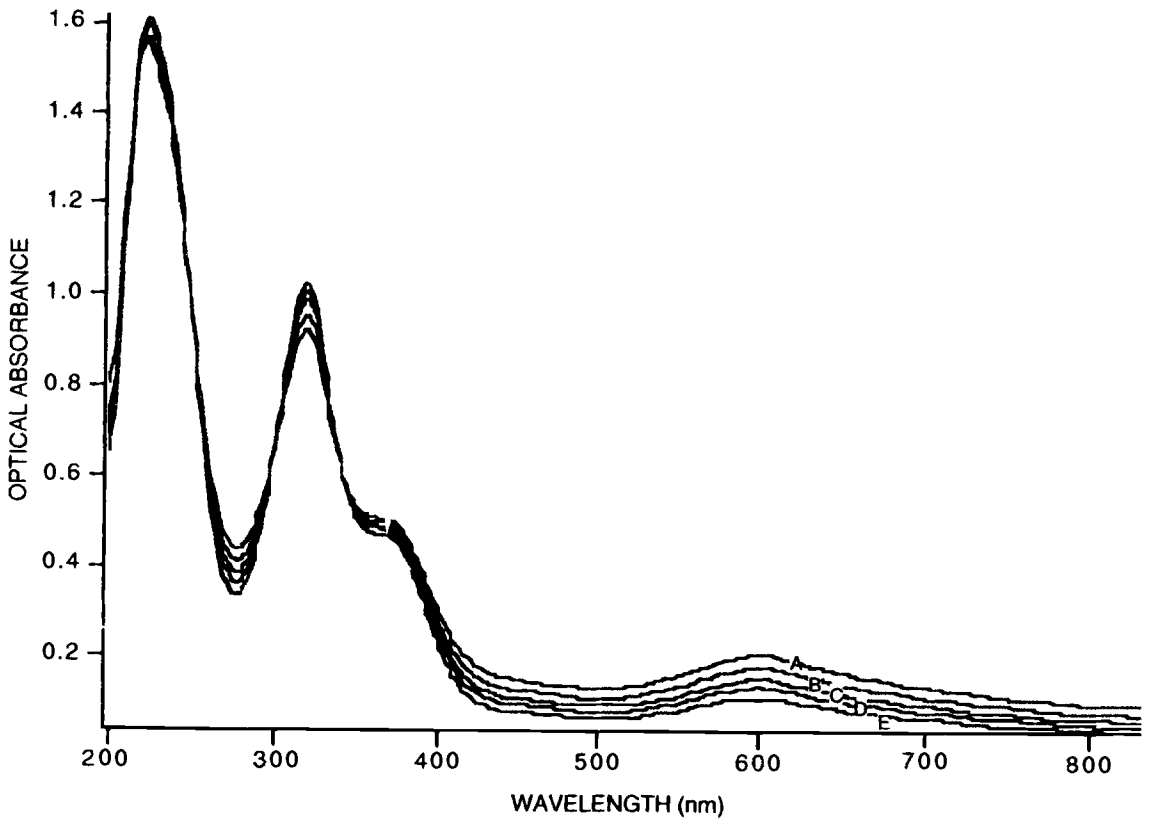



FIG. 5—*Showing the decomposition of the purple lead-THQ complex in 0.5% HCl. Spectra A-E were taken at 1 min intervals starting with A.*

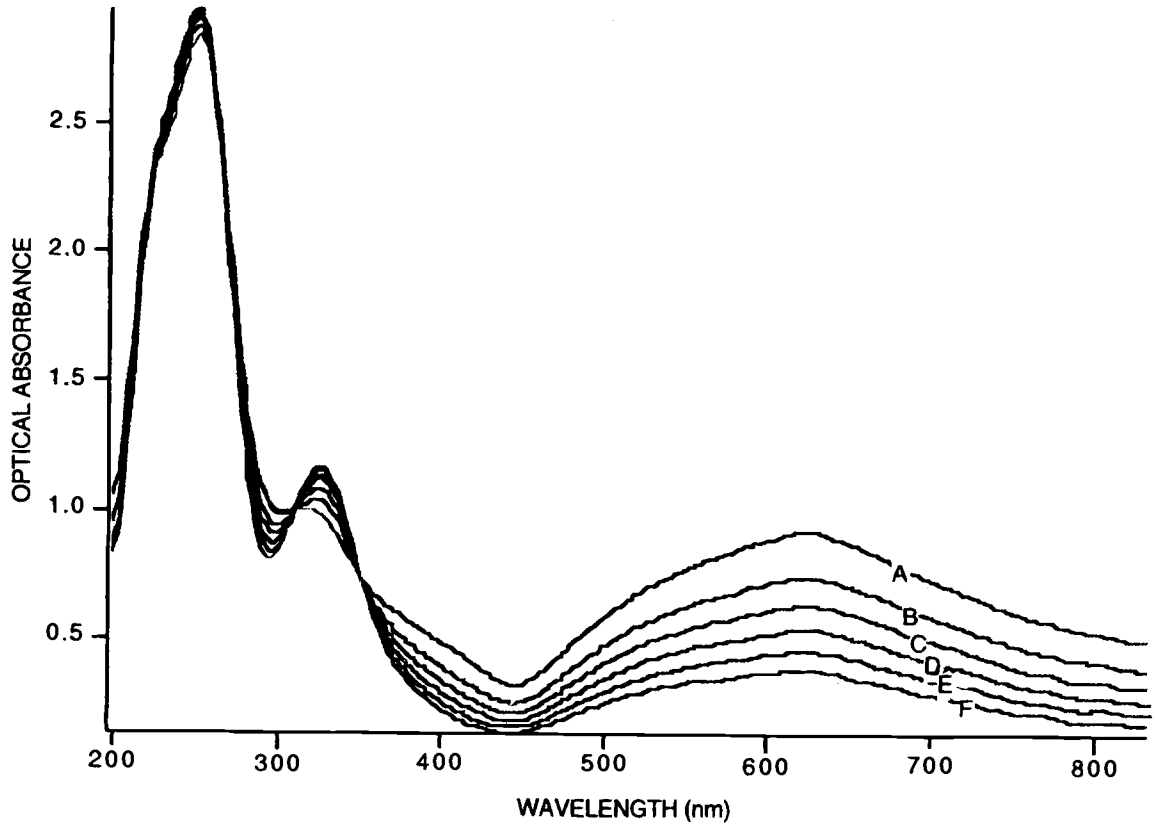



FIG. 6—*Showing the decomposition of the blue-violet lead-rhodizonate complex in 5% HCl. Spectrum A was taken initially followed by B-F at 1 min intervals.*

the buffered solution of about 10 h, which represents a considerable improvement over that for the sodium rhodizonate solution. As will be shown below, the solution of the reagent prepared in this way is just as effective in producing the desired response to lead as solutions of the reagent and the buffer used separately, but because of its greater longevity, its use should facilitate the acquisition of more reproducible results.

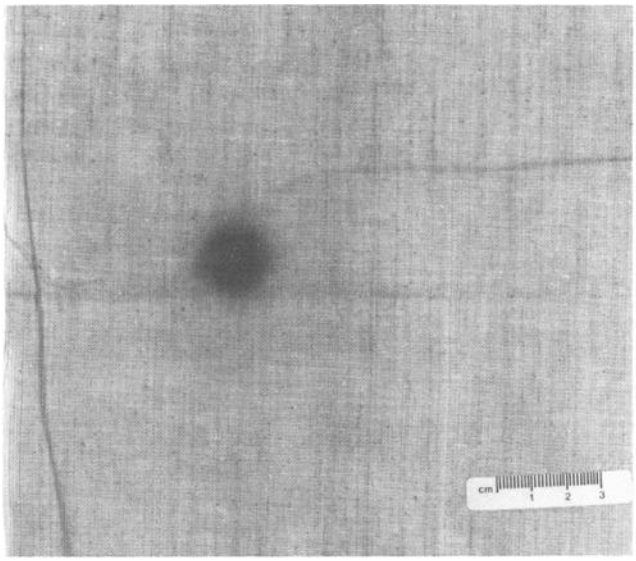
*Nature of the Lead Deposit*

A deposit originating from a firearm discharge can contain two chemically distinct forms of lead: (a) Metallic lead, Pb(0), arising from friction induced transfer of lead from the bullet to the surface which it is penetrating. This might be expected to be significant, for example, around and within a penetration through a piece of wood where there is considerable friction and contact distance, depending on the thickness of the wood, but less so when the penetration is through a thin soft material such as an article of clothing. (b) Ionized lead, Pb(II), present in the gaseous discharge associated with the burning of the primer. This certainly will be significant when the deposit is collected from a surface that was close to the muzzle of the weapon at the moment of firing, but may also be found around more distant penetrations due to condensation of discharge gases on the bullet, while still in the barrel, followed by subsequent transfer onto the surface being penetrated (bullet wipe).

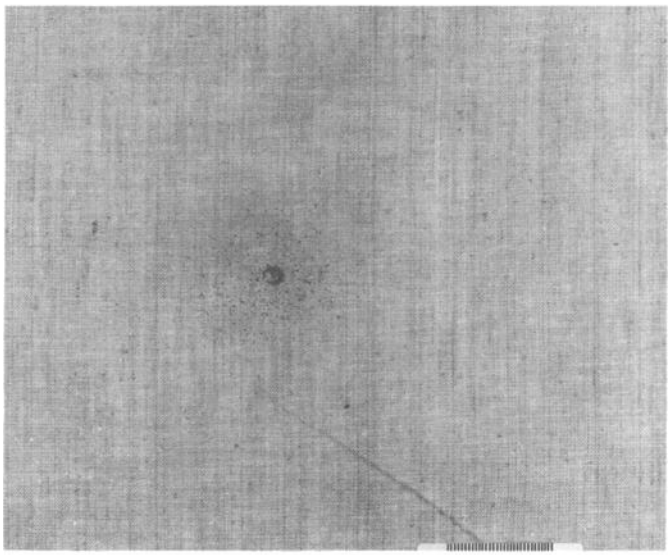
*Detecting Metallic Lead, Pb(0)*

Experiments that we have conducted indicate that treatment of metallic lead first with sodium rhodizonate and then with the pH 2.8 tartrate buffer, or simultaneously with the two solutions, does not produce the desired scarlet complex necessary for onward conversion to the diagnostic blue-violet complex. Instead, an insoluble purple colored complex forms that instantly decolorizes when acidification with 5% HCl is carried out. Because formation of the purple complex alone is not sufficiently diagnostic of lead, its formation is not particularly useful. Although we do not know the complete structure of the purple complex, we have found, through decomposition studies, that it contains tetrahydroxyquinone (THQ) as the coordinating ligand rather than rhodizonate. THQ is the two electron reduction product arising from rhodizonate, shown in Fig. 4, and is presumably produced in response to rhodizonate acting as the oxidizing agent for the two electron oxidation of Pb(0) to Pb(II). The presence of THQ in the purple complex was recognized by spectroscopically monitoring the decomposition of a suspension of the purple complex in 0.5% HCl (Fig. 5). During this decomposition, the visible disappearance of the absorption band at 590 nm arising from the complex is accompanied by an intensification of the bands at 204, 308, and 380 nm, known to originate from THQ by comparison with an authentic sample purchased from Aldrich.

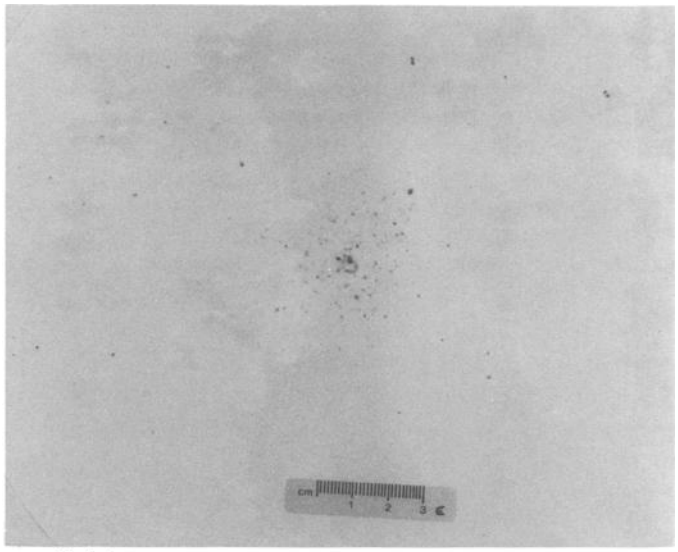
The problem of unwanted expenditure of the available lead in the formation of the purple complex can be overcome by allowing the metallic lead to oxidize to Pb(II) before the sodium rhodizonate or rhodizonic acid solution is applied. This is readily achieved by preacidifying the surface on which the lead is suspected of being present with the pH 2.8 tartaric acid buffer solution and allowing atmospheric oxygen to accomplish the oxidation, which it does, at this pH, over about a 5 min period with lead particles having a mesh size of up to 325. If the lead deposit has been transferred from the original surface using a piece of paper moistened with



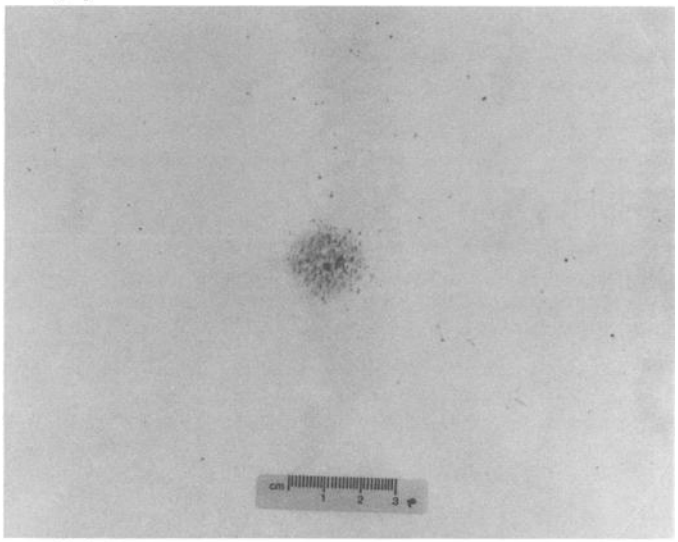
(a) i



(a) ii



(b) i



(b) ii

FIG. 7—*.22 in. LR hollow point lead bullet penetrations in pieces of cloth from a range of 50 mm, (a)i, and 250 mm, (b)i, and the respective lead distribution patterns (a)ii and (b)ii demonstrated by the lead rhodizonate test applied in the manner described in this article. Photographs of the test results were taken three days after the application of the test.*

15% glacial acetic acid, as recommended by Dillon (1), then this will also facilitate the oxidation of any metallic lead. Having oxidized any Pb present as Pb(0), application of the Test can then proceed in accordance with the notes given in the next section.

*Detecting Ionized Lead, Pb(II), and Formation of the Scarlet Complex*

The section above stressed the fact that the Sodium Rhodizonate Test only works as a definitive test for lead when the lead is in the Pb(II) form, as a result of the adverse effect of Pb(0) on rhodizonate. Assuming, then, that any Pb present has been preoxidized to Pb(II), there are two alternative ways that the test can be conducted: (a) spraying with sodium rhodizonate followed by pH 2.8 tartrate buffer as suggested by Dillon (1), or, (b) spraying with pH 2.8 tartrate buffer followed by sodium rhodizonate as suggested by Lichtenburg (2). It can already be seen that the second method has the advantage of presenting the opportunity for any Pb(0) to oxidize to Pb(II), prior to the introduction of the rhodizonate, but, in addition, there are other reasons for favoring it. We have observed that the formation of the unwanted THQ containing purple compound will occur in preference to the scarlet complex in two other circumstances: (a) If the complexation reaction is carried out at neutral pH rather than at pH 2.8 [also reported by Feigl and Suter (6)], and (b) if the buffer used to achieve pH 2.8 is not tartrate based, suggesting that tartrate is in some way involved in the desired reaction. (We have seen some evidence from our solid state $^{13}C$ NMR and laser ablation mass spectroscopic studies that tartrate is incorporated into the product, although it is not clear at this stage how it is incorporated or to what extent.) Thus, treatment of the surface to be examined with the tartrate buffer before applying the rhodizonate solution ensures both that the pH is lowered to the point where the scarlet colored complex will form before complexation commences, and also that the necessary tartrate is present before complexation commences. Application of sodium rhodizonate dissolved in the tartrate buffer appears to

be a satisfactory variation of the second method and has the advantage of using a solution less prone to decomposition than aqueous sodium rhodizonate as noted above. In cases in which the presence of Pb(0) is suspected and needs to be confirmed, it would seem better, however, to pretreat the surface with the buffer before applying either sodium rhodizonate dissolved in buffer solution or freshly prepared aqueous sodium rhodizonate solution.

*Conversion of the Scarlet Complex to the Blue-Violet Complex*

The strength of the Sodium Rhodizonate Test as a definitive test for lead is that a result can only be considered to be positive when two quite different color changes have been noted. Conversion of the initial scarlet complex must be followed by formation of a blue-violet complex upon treating it with 5% HCl if the source of the colors is to be unequivocally concluded as being lead. The problem with the second stage of the test is that, although the scarlet complex transforms to the blue-violet form readily enough, prolonged exposure to the HCl decomposes the blue-violet complex into colorless compounds, and so a permanent record of the positive result can be lost. This is illustrated by the decomposition curves shown as Fig. 6 which illustrate the decay of the visible absorption band at 608 nm as a function of the time of exposure to 5% HCl. As this occurs, the UV bands arising from free rhodizonic acid at 242 and 318 nm intensify.

*Modification of the Test Procedure to Incorporate New Findings*

As already noted, the first stage of the Test is best accomplished by spraying the test area first with the tartrate buffer and then with a freshly prepared saturated aqueous sodium rhodizonate solution or, alternatively, with a single solution prepared by dissolving the sodium rhodizonate directly in the buffer until saturation point is reached. At the second stage, the decomposition of the blue-violet complex can be avoided, very simply by allowing the blue-violet color to develop to its maximum intensity and then removing the excess HCl solution by drying the test area thoroughly with a hair drier. Once free of excess HCl, the blue-violet color remains indefinitely without any obvious fading. This has been demonstrated by performing the test on a series of cloth samples from which a gunshot residue has been transferred using the Bashinski method (1) or by direct application of the reagents. In all cases, the blue-violet coloration that appeared had not deteriorated after a period of nine months. Photographs of typical test results are shown in Fig. 7.

*Acknowledgment*

We are grateful to the Australian National Institute of Forensic Sciences for funding this work and to Mr I. Sarvas (Technical Officer, South Australian Forensic Science Centre) for his assistance with the shooting experiments.

## References

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# ERRATA

**ERRATUM 1**

The word "*Rea*" was inadvertently transposed as "*Era*" in the Table of Contents for the paper "Sleepwalking Disorder and *Mens Rea*: A Review and Case Report" published in the Journal of Forensic Sciences 1997;42(1):17–24 by Thomas N. Thomas.

**ERRATUM 2**

The correct labeling for the Figure 7 of the paper "An Update on the Use of the Sodium Rhodizonate Test for the Detection of Lead Originating from Firearm Discharges" published in the Journal of forensic Sciences 1996;41(6):1046–1050 by Michael R. Bartsch et al. Should be as follows:

(a)ii should be (b)i
(b)i should be (b)ii
(b)ii should be (a)ii