

TECHNICAL NOTE

Malcolm D. McGinnis,¹ M.S.; John I. Thornton,¹ D.Crim.; and Edgar O'N. Espinoza,¹ M.P.H.

Dithizone as a Microcrystalline Test for the Confirmation of Projectile Lead Wipes

REFERENCE: McGinnis, M. D., Thornton, J. I., and Espinoza, E. O'N., "Dithizone as a Microcrystalline Test for the Confirmation of Projectile Lead Wipes," *Journal of Forensic Sciences*, JFSCA, Vol. 32, No. 1, Jan. 1987, pp. 242-244.

ABSTRACT: The dithizone test is frequently used as a color test for lead in the confirmation of projectile wipes. An adjustment of test conditions will also allow the dithizone reaction to be conducted as a *microcrystalline* test, thereby increasing the specificity of the reaction. The color resulting from the formation of the inner salt complex between dithizone and the lead cation is maintained, and may be observed on the characteristic crystals obtained.

KEYWORDS: forensic science, ballistics, lead (metal), dithizone, crystallography

In shooting cases, it is occasionally of investigative interest to establish the trajectory of a bullet where the projectile has perforated an object by confirmation of a lead wipe. In many forensic science laboratories, the dithizone (diphenylthiocarbazone) test is used for this purpose. Although the dithizone test gives a reasonably characteristic color reaction with lead [1], it does in fact react in some manner with virtually all of the elements from Column 6 (VIa) to Column 16 (VIb) of the periodic chart, some 33 elements in all [2]. Of these, thallium, manganese, silver, zinc, mercury, bismuth, and lead give *some* shade of red or pink. The test may therefore be criticized on the basis of the common charge leveled against *any* color test, that the test is subjectively interpreted, and as a consequence, lacks specificity. This argument (which, parenthetically, the present authors view as unfair) may be addressed by using the dithizone test as a *microcrystalline* test in addition to a color test. To do so requires a different formulation of the test reagent from the classical 0.001% solution of dithizone in carbon tetrachloride [3].

Other microcrystalline tests of course exist for lead, but typically they are a bit tricky and require very precise adjustment of test conditions [4]. The test with potassium iodide (KI) results in the precipitation of characteristic crystals of lead iodide (PbI₂), but PbI₂ is soluble in an excess of KI with the formation of the PbI₂ · KI · 2H₂O double salt. The test with

Received for publication 18 Feb. 1986; revised manuscript received 20 March 1986; accepted for publication 21 March 1986.

¹Graduate student, professor of forensic science, and graduate student, respectively, Forensic Science Group, Department of Biomedical and Environmental Health Science, University of California, Berkeley, CA.

hydrochloric acid (HCl) results in the precipitation of characteristic crystals of lead chloride (PbCl_2), but the test drop must be optimally acidified with nitric acid (HNO_3). In addition, the temperature of the test drop is of concern, as PbCl_2 is quite soluble in warm aqueous solution and there exists the possibility that the HNO_3 will react exothermically with water and warm the test drop. The test with mixed acetates and potassium nitrite (KNO_2) precipitates characteristic crystals of the triple nitrite $2\text{KNO}_2 \cdot \text{Cu}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2$, but again the precipitate is soluble in an excess of alkali nitrite.

Experimental Procedure

A few milligrams of the material to be tested for metallic lead is excised or scraped into a 10- by 75-mm culture tube and approximately 2 mL of concentrated HNO_3 added. The tube is heated in a hot water bath for a few minutes to dissolve the metallic lead. The acid extract is then decanted into a 5-mL flask and evaporated to the point of dryness on a hotplate. Two drops of 0.1N HNO_3 are added and stirred to take up any residue present. One drop of the 0.1N HNO_3 is then removed and placed on a microscope slide. One drop of a 1% solution of dithizone in pyridine is placed on the microscope slide in close proximity to the test drop. The reagent drop is drawn into the test drop and the preparation examined under the microscope at $\times 100$.

Results and Discussion

The procedure described above gives characteristic, but easily distinguishable, crystals with lead and mercury. The colors observed on the crystals with these two elements as seen by transmitted light microscopy are identical to those observed when the test is run as a color test; the colors are therefore distinguishable. No crystal formation was observed with bismuth, cadmium, cobalt, silver, tin, manganese, thallium, or zinc. Lead gives characteristic aggregations of long narrow blades, as illustrated in Fig. 1. Mercury gives large, thin, branched needles which are totally dissimilar to those observed with lead.



FIG. 1—Characteristic crystals of lead with dithizone.

It is not feasible to use the classical dithizone reagent, that is, a 0.001% solution of dithizone in carbon tetrachloride, as a microcrystalline reagent for lead. Carbon tetrachloride is much too volatile to permit the formation of characteristic crystals, it is immiscible with acidic aqueous solutions of lead extracted from a suspected lead wipe, and a 0.001% solution of dithizone is too dilute for an effective microcrystalline test. (The deep green color of solutions of dithizone in carbon tetrachloride belies its low solubility; the solubility of dithizone in carbon tetrachloride is only 0.5 g/L at 20°C [5]. The final and probably most important reason to reject carbon tetrachloride is that the inner salt complexes formed by dithizone and many metals are virtually insoluble in water, but are quite soluble in carbon tetrachloride. This is precisely why carbon tetrachloride is used in the color test and for solvent extraction, but is the opposite of what is needed for a microcrystalline test.

In the present study, pyridine was found to be a satisfactory solvent. Pyridine is one of the few solvents in which dithizone is freely soluble, it is miscible with aqueous solutions of the test cation, and it is not excessively volatile. A 1% solution of dithizone in pyridine was found to be optimum; 0.1 and 0.01% solutions were evaluated and found to be less efficacious. This represents a thousandfold increase of dithizone over the concentration of dithizone in carbon tetrachloride when the test is run as a color reaction.

The test is sensitive to 10 μg of lead with respect to the formation of crystals; to perceive a color to the crystals, the concentration of lead must approach 25 μg .

References

- [1] Jungreis, E., *Spot Test Analysis*, Wiley, New York, 1985.
- [2] Irving, H. M. N. H., *Dithizone*, Chemical Society, London, 1977.
- [3] Feigl, F., *Spot Tests in Inorganic Analysis*, Elsevier, New York, 1958.
- [4] Chamot, E. M. and Mason, C. W., *Handbook of Chemical Microscopy*, Vol. II, 2nd ed., Wiley, New York, 1948.
- [5] Iwantscheff, G., *Das Dithizon und seine Anwendung in der Mikro- und Spuren-analyse*, 2nd ed., Verlag Chemie, Weinheim, 1972.

Address requests for reprints or additional information to
Dr. John I. Thornton
Forensic Science Group
Department of Biomedical and Environmental Health Sciences
University of California
Berkeley, CA 94720