

TECHNICAL NOTE

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A Thin-Layer Chromatographic Procedure for Confirming the Presence and Identity of Smokeless Powder Flakes

REFERENCE: Peak, S. A., "A Thin-Layer Chromatographic Procedure for Confirming the Presence and Identity of Smokeless Powder Flakes," *Journal of Forensic Sciences*, JFSCA, Vol. 25, No. 3, July 1980, pp. 679-681.

ABSTRACT: A simple and inexpensive procedure to confirm the identity of unburned or partially burned flakes of smokeless powder is described. The procedure is based on (1) particle morphology and solubility in acetone, (2) R_f values of the flakes when they are chromatographed on thin-layer chromatographic plates, and (3) specificity of the visualizing reagent to nitrite.

KEY WORDS: criminalistics, chromatographic analysis, gunshot residues

Unburned or partially burned flakes of smokeless powder are occasionally found on the hands of gunshot suicide victims² and, though rarely, on the hands of live suspects in a shooting incident. There are two types of smokeless powder: single-base powder, which consists of nitrocellulose and stabilizers, and double-based powder, which also contains up to 40% by weight nitroglycerine.

A simple and inexpensive procedure has been designed to confirm the identity of these flakes. The Saltzman-Greiss reagent [1] used in the procedure tests for nitrite ions released from nitroglycerine (NG) and nitrocellulose (NC) by alkaline hydrolysis. Increased specificity is obtained by sequential chromatography on thin-layer silica gel plates, using solvent systems that separate NC from NG and distinguish propellant-grade NC from nonpropellant-grade by differences in the length of the cellulose polymer chain. Nonpropellant NC is used as a base for some lacquers, inks, resins, and films.

Materials

For the Saltzman-Greiss reagent [1], a stock solution of 0.1% by weight *N*-(1-naphthyl) ethylenediamine dihydrochloride in distilled water was prepared. Eighty millilitres of the

This work was supported under a contract with the Law Enforcement Assistance Administration, U.S. Department of Justice. Received for publication 17 Aug. 1979; revised manuscript received 29 Nov. 1979; accepted for publication 5 Dec. 1979.

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distilled water solution was used to dilute 14 mL of glacial acetic acid, then 0.5 g of sulfanilic acid was dissolved in the solution, and finally distilled water to a volume of 100 mL was added. The prepared reagent is stable for one or two weeks if it is stored in a brown bottle away from light.

The chromatographic solvent used to separate NC and NG consisted of toluene/petroleum ether/ethyl acetate in the ratio 12:12:1. (Benzene was originally used, but recent restrictions on the use of benzene for health reasons led to the use of toluene, which is equally effective.) The boiling point for the petroleum ether ranged from 35 to 60°C.

Propellant-grade NC was identified by using a chromatographic solvent consisting of Methyl Cellosolve®/95% ethanol (15:85).

Schleicher & Schuell silica gel G1500, 250 μm thick on glass-backed plates, was used. The plates were cut to a convenient size, such as 10 by 10 cm, and were activated by being heated for 30 min at 100°C. Use of powdered thin-layer chromatographic (TLC) silica gel, such as silica gel 60, 70-230 mesh (E. Merck Reagents, Darmstadt, Germany), is optional.

Two standard solutions for NG were prepared: 0.1 and 0.01 mg/mL in reagent-grade acetone. The standard solution for NC consisted of 1 mg/mL in acetone. Du Pont DHB14P was used for the nonpropellant-grade NC standard, and single-base smokeless powder for the propellant-grade. Norma .38 Special or .357 Magnum cartridges are convenient sources for a small quantity of single-base propellant powder. Du Pont SR and IMR series powders are also single-base.

Other materials required for the procedure included 0.1*N* sodium hydroxide, fine-pointed forceps (such as Dumont #5), small vials or containers with tight lids (such as 1.5-mL Eppendorf centrifuge tubes), and sprayer-atomizers (such as the "Chromist" spray unit from Gelman Instrument Co.). A metal disk covered with Scotch #65 transfer tape was used to remove particles from hands.

Procedure

Inspect the hand for visible smokeless powder flakes with a hand lens. Flakes larger than 0.1 mm are visible. With forceps, transfer the flakes to a vial and seal the vial. Then, with transfer tape, sample the hand in the usual manner, that is, including web, fingers, back of the hand, and wrist.

Transfer the flakes from the vial a TLC plate with forceps. Place individual flakes separately at the origin. Spot each particle twice with 5 to 10 μL of acetone to dissolve the flakes. Badly charred or burned flakes will not dissolve and generally cannot be tested by this procedure. When more than ten flakes are available, an alternative method for transferring the collected flakes is to first suspend them in acetone. To do this, add 50 μL acetone to the vial and mix thoroughly in a vortex mixer. Make sure the flakes are swept off the sides of the vial into the solvent. Evaporate to about 10 μL by uncapping the vial, and put 5 μL of the concentrated sample on the plate.

Examine the tape under a low-power microscope (7 to 10 \times). Transfer to the TLC plate any easily removable particles that appear yellowish to yellowish green or pale tan to light brown. These particles are usually irregular in shape. Forceps and a fine-pointed probe are suitable transfer tools. Spot the particles twice with 5 to 10 μL of acetone to dissolve them.

Spot 1 μL of each standard on the plate. For Step 1, chromatograph the plate for 2.5 cm in the Methyl Cellosolve/ethanol solvent. Mark the front and allow the solvent to dry. For Step 2, rechromatograph the plate for 5.0 cm in the toluene/petroleum ether/ethyl acetate solvent. Mark the front and allow the solvent to dry.

Spray the plate lightly but thoroughly with 0.1*N* sodium hydroxide and immediately dry it at 100°C for 6 min. This procedure hydrolyzes NO_2^- groups from the parent compound while minimizing diffusion. After the plate cools, spray it with the Saltzman-Greiss reagent. The presence of NO_2^- initiates a diazo coupling in the visualizing reagent. Positive reac-

tions are pink, and highly concentrated samples have a yellow center with a pink halo. The lower-limit sensitivity of the reagent for NG is 10 ng/sample and for NC, 500 ng/sample.

Note the presence and position of the spots. Allow the plate to dry for 1 or 2 h away from light. A warm oven (37°C) is suitable although not necessary. The visible reaction spot usually fades as the plate dries.

Photograph by contact photography with a high-contrast, red-insensitive film (such as Kodak Professional Film 7302). An enlarger is a suitable light source. With the light source distance at 88 cm, the exposure time is 5 s at f/11. The positive reaction spots appear as light spots on the negative and can often be photographed 24 h after plate visualization even when they are no longer visible to the eye. It is necessary to protect the plate from light. Once the background turns pink the plate is no longer useful for photography.

Results

Step 1 of the chromatographic procedure distinguishes propellant from nonpropellant nitrocellulose. In 15% Methy Cellosolve in ethanol, most of the propellant-grade NC remains at the origin, with a small amount moving with the solvent front. For nonpropellant NC the process is reversed; most of the NC moves with or just behind the solvent front.

Step 2 of the procedure distinguishes NG from nonpropellant NC. During Step 1, NG moves with the solvent front, as does NC with a short cellulose polymer chain. In the toluene/petroleum ether/ethyl acetate solvent, NG chromatographs with an R_f value of 0.3 while NC remains stationary [2].

Optional Rapid Screening Procedure

When a rapid screening procedure is desired, the following method can be used if the tape sample is not to be used for additional tests.

Dust the tape with loose TLC silica gel and lightly tap off the excess gel. Spot the surface of the tape with 2- μ L aliquots of acetone until the entire surface is covered. The silica gel prevents diffusion of low concentrations of NG and NC. Spray the tape lightly (do not wet!) with 0.1N sodium hydroxide, dry for 6 min at 100°C, cool, and spray lightly with Saltzman-Greiss reagent. Examine the tape under a low-power microscope for pink areas (positive reaction).

References

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