Forensic Science International 278 (2017) 24–31

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

The use of unburned propellant powder for shooting-distance determination. Part II: Diphenylamine reaction

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ARTICLE INFO

Article history:
Received 4 April 2017
Received in revised form 13 June 2017
Accepted 19 June 2017
Available online 27 June 2017

Keywords:
Transfer
Organic solvent
TLC-plate
Chemical reaction
Density

ABSTRACT

Shooting samples were produced on standard textile pats of six different ammunition types: four ammunitions with exclusively infrared luminescent propellant powder particles, one containing a mixture of luminescent and non-luminescent particles and one with only non-luminescent particles. Unburned propellant powder particles in the gunshot residue (GSR) on the textile of each sample were transferred onto TLC-plates with the aid of an organic solvent. The patterns of the partially and the all-luminescent propellant powder residue on the TLC-plates were visualized in the near infrared wavelength range by the aid of an IR-sensitive camera. The transfer TLC-plates of all six ammunition types were sprayed with a diphenylamine solution, which reacts with the nitrate groups of the nitrocellulose and nitroglycerine and produces deep blue dots thereof.

A series of samples with different shooting distances produced with one of the ammunition types was used for the shooting distance determination study. Transfer on TLC-plates was performed and pictures of the plates were taken before and after the chemical reaction. An imaging software was used to measure the density of the particles on the transfer TLC-plate pictures within a defined area around the bullet hole. Curves were drawn with the particle density data vs. the shooting distance.

It has been shown, that the transfer of the particles onto a TLC-plate and the chemical reaction eliminate the limitations of the IR-method presented in Part I. Therefore, this method allows shooting distance determination at any textile and for any ammunition type as soon as unburned propellant powder particles are left on the target tissue.

1. Introduction

Conventional inorganic gunshot residues (GSR) consist of heavy metal such as lead, antimony and barium [1,2]. These target molecules for inorganic GSR-analysis are not present in sintox ammunition. A common component in any ammunition is nitrocellulose (NC) which is the main propellant powder product [3]. The only exception is black powder ammunition, which is almost not relevant for forensic case work.

About 80% of the ammunition contain propellant powder with IR-luminescent components [4]. The unburned propellant powder particles of such ammunition can be detected by infrared imaging [5]. The shooting distance can be determined by the quantification of the particle distribution and an ammunition specific particle density vs. shooting distance curve [4]. The limits of this method are:

- About 20% of the ammunition do not contain luminescent propellant powder.
- In some propellant powders only part of the particles are luminescent; the non-luminescent ones are not detected.
- The target tissue can be IR-luminescent at the same optical conditions as the propellant powder. Therefore, the propellant powder particles cannot be detected.
- Fibers within or on the textile may also be IR-luminescent and, therefore, are not differentiated from propellant powder particles. An error in the shooting distance determination will be the consequence.

To overcome the problem of luminescent textiles and/or luminescent fibers, the propellant powder particles were transferred from the target textile onto an optically inactive and chemically inert material (TLC-plate) by the aid of an organic solvent. As most textile materials and fibers as well as inorganic compounds do not dissolve in organic solvents, only nitrocellulose

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http://dx.doi.org/10.1016/j.forsciint.2017.06.022
0379-0738/

and its additives are transferred. IR images were taken from the transfer TLC-plates with a IR-sensitive camera.

Compared to the method described in Part I, we enlarged the study to enable organic GSR detection and shooting distance determination for any ammunition type (except black powder ammunition). For this purpose, we added a chemical reaction with diphenylamine to the optical IR-luminescence detection technique. Diphenylamine has already been used in the past for gunpowder residue detection studies [6]. Due to its non-specific reaction, no such method did establish itself in the forensic gunshot residue analysis so far. Diphenylamine solution is sprayed on the transfer TLC-plates. Nitrite and nitrate ions (from the nitrocellulose) react with diphenylamine. In a first oxidation step, it dimerizes to *N,N′*-diphenylbenzidine which subsequently oxidizes to a deep blue diimine system (Scheme 1). Pictures of the TLC-plates were taken with a regular digital camera.

The performance and the advantage of the particle transfer from the target textile to a TLC-plate are presented in picture series of different ammunition types showing the IR-picture of the target textiles and of the transfer TLC-plate as well as the picture at normal optical conditions of the TLC-plate after the chemical reaction.

The target textiles of one shooting distance series already presented in Part I was further analyzed with the transfer as well as the diphenylamine reaction method. Instead of counting the amount of transferred particles – as reported in Part I –, the pictures of both the IR-sensitive camera and the regular camera were analyzed by an imaging software, giving the pixel saturation in a predefined area around the bullet hole. The pixel saturation corresponds to the particle density within this area. Shooting distance curves are drawn with both data sets.

2. Material and method

The following material was used:

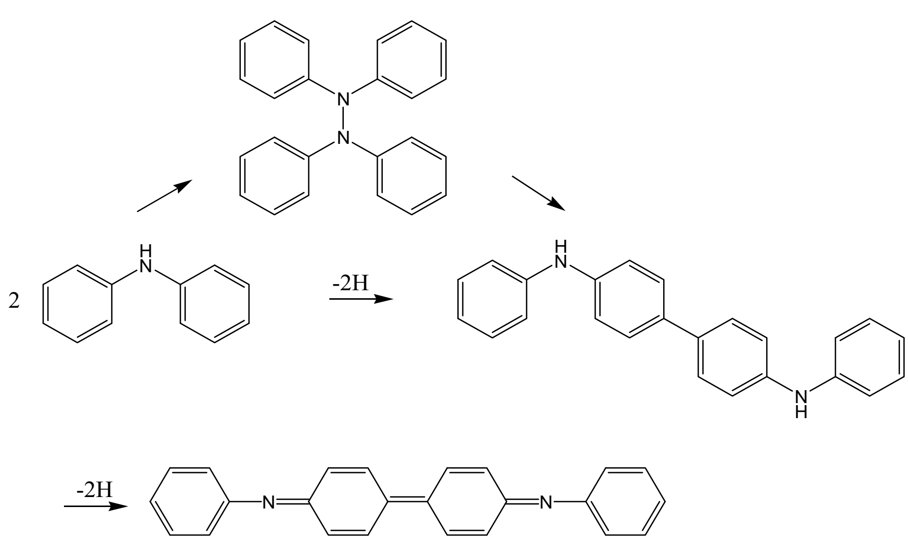
Ammunition:	GECO, 9 mm Luger, 124 grain, super clean; all-luminescent propellant powder
	RUAG, 9 mm Luger, 147 grain, (SWISS P Subsonic); all-luminescent propellant powder
	RUAG, 9 mm Luger, (PP 41); all-luminescent propellant powder
	S&B (Sellier & Bellot), 9 mm Luger, NONTOX; all-luminescent propellant powder
	S&B, 9 mm Luger, 124 grain; partially luminescent propellant powder
	Fiocchi, 9 mm Luger, 123 grain; completely non-luminescent propellant powder

Gun:	Pistol, Beretta, model 92 FS, cal. 9 mm Luger
Textile:	White standard textile (100% cotton, 27 cm broad roll, 210–220 g/m^2) for towel automat Solidcare, RVR Service AG, Switzerland
Samples:	Textile patches of ca. 21 × 27 cm were fixed on a cardboard underlay and positioned perpendicular to the muzzle. A series of pistol shooting samples with shooting distances of 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, and 300 cm was produced with GECO ammunition (same as in Part I). In addition, two pistol shooting samples were produced with the other 5 ammunition types (see above), each at shooting distances of 40 and 60 cm.
Detection unit a:	Infrared-sensitive digital camera Fuji X-T1 equipped with a 725 nm longpass filter INFRARED (R72) from HOYA. Pictures of the target textiles and of the transfer TLC-plate (before the diphenylamine reaction) were taken at bright spotlight of 590 nm produced by a RAFIN Polilight PL 500.
Detection unit b:	Digital camera Nikon D3x for the imaging of the propellant powder distribution on the TLC-plate after the diphenylamine reaction.
Power press:	Hydraulic power press machine CMC Italia s.r.l., 130 bar (oil stamp pressure), bed and ram bottom size 40 × 52 cm, resulting pressure = 17.7 N/cm^2
Styrofoam®:	Expanded polystyrene plates: 40 × 52 × 2 cm, strength at 2 mm compression = 20 N/cm^2
Cardboard:	Regular cardboard: 21 × 29 × 0.2 cm
TLC-equipment:	Plates: TLC-ready-to-use layers SIL G-25, 20 × 20 cm, glass, Carl Roth, Germany
	Spray cabinet: Camag
	Spraying device, glass (as for post-chromatographic derivatization)
Chemicals:	Transfer solvent: ethylacetate p.a. from SIGMA–ALDRICH
	Reagent: 2% diphenylamine dissolved in 70% sulfuric acid (diphenylamine p.a. from FLUKA; sulfuric acid p.a., 95–97%, from MERCK, diluted with distilled Water, produced in-house).
Software:	SDP-ColorFinder® 4.4 — expert from Schulz Digitale Projekte, Magdeburg (Germany), was used to determine the distribution of propellant powder particles.

Pistol shooting samples were produced with the six ammunition types on standard textile patches as described above and pictures were taken with the IR-sensitive camera.

The transfer of the propellant powder particles was performed as follows (each sample separately):

- The sample is positioned beneath a power press as described in Scheme 2.
- A TLC-plate is dipped in ethylacetate for a few seconds to allow a complete solvent penetration into the silica layer. The TLC-plate



Scheme 1. Oxidation of diphenylamine to the deep blue diimine.