Science and Justice 55 (2015) 467–471

Contents lists available at ScienceDirect

Science and Justice

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

Novel method for the detection of nitroglycerin in smokeless powders

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ARTICLE INFO

Article history:
Received 4 May 2015
Received in revised form 11 August 2015
Accepted 22 August 2015

Keywords:
Smokeless powder
Nitroglycerin
Spot test
Dimethylaminocinnamaldehyde

ABSTRACT

Nitroglycerin is an active component in many explosive substances. Notably, it is found as an active ingredient in double-base smokeless powders, differentiating them from single-base powders, whose main active ingredient is nitrocellulose. It is proposed that the detection of nitroglycerin within various types of ammunition will allow for the differentiation between single and double-base smokeless powders, thus allowing for a method of distinguishing ammunition or bulk powder samples that may be found during the course of a criminal investigation. Presumptive tests are an effective tool in field-testing for forensic science. These tests are used primarily as rapid, sensitive means of elucidating the chemical characteristics of an unknown sample *in-situ*. In this paper, the authors present a novel method for the detection of nitroglycerin in smokeless powders with the use of a presumptive color test reagent, dimethylaminocinnamaldehyde (p-dmac). Twenty-five smokeless powders were tested using this reagent to evaluate the color change that would occur in the presence of nitroglycerin. All presumptive results were confirmed *via* gas chromatography–mass spectrometry.

1. Introduction

Smokeless powders are propellants commonly found in ammunition and may also be encountered in improvised explosive devices (IEDs). Single, double, and triple-base powders are characterized by the main active ingredients. Single-base powders contain nitrocellulose (NC). Double-base powders contain a mixture of NC and nitroglycerin (NG). Triple-base powders, typically limited to military ordinance, contain NC, NG, and nitroguanidine [1–5]. In addition to the presence of NG as a primary propellant, NG may also be added as an additive to enhance the properties of the ammunition of double or triple-base powders only. Propellants may also contain a myriad of additives, such as stabilizers, lubricants and plasticizers, as well as chemical constituents to control burn rate and suppress muzzle flash. The presence of trace components may be the result of the manufacturing process [5].

Routine forensic laboratory examinations of the organic composition of smokeless powders and ammunition can be beneficial as they can deliver probative information concerning powder type and possible source attribution [6]. Differentiating between single-base and double-base powders offers at least more identifier, which can further an investigation. Previous studies have focused on the use of p-dimethylaminocinnamaldehyde (p-dmac) as a presumptive test for urea and urea nitrate [7–9]. The reliability of p-dmac as a presumptive test for the detection of nitroglycerin in smokeless powders was investigated.

The selected reagent for the presumptive test, p-dmac, has been shown to exhibit a color change in the presence of urea nitrate [10]. In a neutral solution, p-dmac will change from orange to red when exposed to urea nitrate. Due to its presumptive nature, the color test results are only preliminary and must be confirmed by instrumental analyses such as mass spectrometry, infrared spectroscopy, or X-ray diffraction [11–17]. It is proposed that this reagent will also serve as an effective means of detecting the presence of NG, thereby allowing for the differentiation of double-base powders from single-base powders. This method would prove beneficial in both *in-situ* and *ex-situ* situations and has great potential for supplementing SOPs due to its speed, reproducibility, and affordability.

Various smokeless powders were subjected to p-dmac to evaluate the ability of the reagent to be employed as a reliable presumptive color test for the detection of nitroglycerin. Resultant color changes were recorded and compared, and the composition of the smokeless powders was initially obtained from the manufacturer MSDS sheet, where available. Gas chromatography–mass spectrometry (GC–MS) was performed as a confirmation test to verify the presumptive test results.

2. Materials and methods

2.1. Color test of ammunition powder

Twenty-five smokeless powders were donated for analysis (Table 1). Approximately six to ten pellets of each were placed into Eppendorf tubes. 500 μL of reagent grade AGS acetone commercially purchased from Pharmco-aaper were added to each Eppendorf tube

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http://dx.doi.org/10.1016/j.scijus.2015.08.001
1355-0306/

Table 1
Ammunition single/double smokeless powder designation.

Powder	Smokeless powder designation (from MSDS)
Hercules 19 Reloder	Double
Hercules Bullseye	Double
Hercules 2400	Double
Hercules #7 Red Dot	Double
Hercules 15	Double
Hercules Green Dot	Double
Hercules Blue Dot	Double
Hercules #45	N/A
Hodgdon Magnum Rifle	N/A
Hodgdon H4831 Rifle	Single
Hodgdon H110	Double
Herter 160	N/A
Herter 162	N/A
Dupont/IMR ss 8081xx	Double
Dupont/IMR 4064	Single
Dupont/IMR 4198	Single
Dupont/IMR 4350	Single
Dupont/IMR SR4759	Single
Brenner 12G	N/A
Remington	N/A
American Eagle Federal	N/A
English Powder	N/A
Winchester Flat Ball	Double
Alliant Unique	Double
NIST 8107	Double

and vortexed. 25 μL of each solution was placed on a glass slide inside a glass ring with an outer diameter of 22 mm. HPLC grade p-dmac was purchased commercially through Sigma-Aldrich. 25 μL of a saturated of p-dmac solution was prepared in reagent grade ACS methanol, purchased commercially from Pharmco-aaper. This solution was added to the smokeless powders. The microscope slide was immediately placed onto a pre-heated hotplate at 70 °C. All reactions were observed over a 5-minute period. The reaction reached completion within 3 min. NG was traditionally prepared and subsequently analyzed in conjunction with the test samples.

2.2. Instrumentation

Approximately 200 cm^3 of each powder was placed into an Eppendorf tube. Each powder was diluted in 750 μL of reagent grade ACS acetone, purchased commercially from Pharmco-aaper, and vortexed. The supernatant was analyzed on an Agilent 7890B gas chromatograph coupled with an Agilent 5977A mass spectrometer. The GC column was an Agilent HP-5MS 5% phenyl methyl silox and helium was the carrier gas. GC conditions were as follows: injector temperature 150 °C; column temperature held at 100 °C for 3 min, heated to 250 °C at a rate of 10 °C/min and held for 5 min at 250 °C; scan range 25 to 500 m/z; and scan rate 3.1 scans/s. Injections were carried out on a split mode with a ratio of 150:1. The injected sample volume was 1 μL. A NG standard control was traditionally prepared and analyzed under similar conditions to the test samples.

Fig. 1. A) Left-most spot test with double-base powder. B) Middle spot test with reagent control. C) Right most spot test with single-base powder.

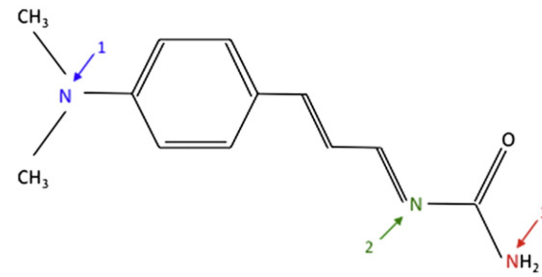

Fig. 2. Structure of free base p-dmac.

2.3. Quantitation

Three powders were chosen for quantitation purposes: Hercules Bullseye, Dupont 8081xx, and Alliant 2400. Fifteen separate, pellets of each powder were placed into individual Eppendorf tubes. Each sample was prepared and analyzed according to the method in Section 2.2.

3. Results and discussion

3.1. Color test

Upon application of the reagents, positive single or double-base powder designations could be made for all 25 samples tested. All single-base powders, when reacted with p-dmac, produced a yellow colored spot (Fig. 1C). All double-base powders, when reacted with p-dmac, produced a fuchsia colored spot (Fig. 1A). It is believed that the detection is caused by the interaction of the N3 and N2 of the free base with two of the oxygen of any of the nitro moieties on

Table 2
Ammunition color test & GC/MS results.

Powder	Color observed (ammo + p-dmac)	NG identification by GC–MS
Hercules 19 Reloder	Fuchsia	+
Hercules Bullseye	Fuchsia	+
Hercules 2400	Fuchsia	+
Hercules #7 Red Dot	Fuchsia	+
Hercules 15	Fuchsia	+
Hercules Green Dot	Fuchsia	+
Hercules Blue Dot	Fuchsia	+
Hercules #45	Fuchsia	+
Hodgdon Magnum Rifle	Yellow	−
Hodgdon H4831 Rifle	Yellow	−
Hodgdon H110	Fuchsia	+
Herter 160	Fuchsia	+
Herter 162	Fuchsia	+
Dupont/IMR ss 8081xx	Fuchsia	+
Dupont/IMR 4064	Yellow	−
Dupont/IMR 4198	Yellow	−
Dupont/IMR 4350	Yellow	−
Dupont/IMR SR4759	Yellow	−
Brenner 12G	Yellow	−
Remington	Fuchsia	+
American Eagle Federal	N/A	+
English Powder	Yellow	−
Winchester Flat Ball	Fuchsia	+
Alliant Unique	Fuchsia	+
NIST 8107	Fuchsia	+
Nitroglycerin	Fuchsia	+

Positive control +: NG detected, −: NG not detected.