Forensic Science International 279 (2017) 140–147

Contents lists available at ScienceDirect

Forensic Science International

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

Technical Note

# An investigation into artefacts formed during gas chromatography/mass spectrometry analysis of firearms propellant that contains diphenylamine as the stabiliser

Paul Pigou[a,b], Genevieve H. Dennison[a], Martin Johnston[a], Hilton Kobus[a,*]

[a] College of Science and Engineering, Flinders University, PO Box 2100, Adelaide, SA 5001, Australia
[b] Forensic Science South Australia, 21 Divett Place, Adelaide, SA 5000, Australia

ARTICLE INFO

*Article history:*
Received 16 November 2016
Received in revised form 14 August 2017
Accepted 14 August 2017
Available online 24 August 2017

*Keywords:*
Gunshot residue
Firearms propellant analysis
Forensic chemistry

ABSTRACT

In the course of providing assistance to legal counsel in a matter that involved the analysis of firearms propellant by gas chromatography/mass spectrometry it was noticed that phenoxazine was reported as a component of 0.22 calibre propellant that contained diphenylamine as the stabiliser. The research was conducted to find how phenoxazine was formed. The results showed that the compound was not phenoxazine but a diphenylamine derivative 4-(phenylimino) cyclohexa-2,5-dien-1-one that formed in the injection port of the gas chromatograph. In addition a second artefact was found to form in the ion source of the mass spectrometer. While the presence of the artefacts does not affect the ability to identify particles as propellant they may impact on comparison with source ammunition.



## 1. Introduction

Firearm propellant particles vary widely in colour, morphology and composition between different calibres of ammunition and between manufacturers. Their shape can include balls, flattened balls, disks, tubes and rods and colours can include green, yellow, grey and white [1]. Propellant particles are often coated with a layer of graphite as an external lubricant and therefore will appear black, with the underlying colour only revealed when the coating is removed. The bulk of the chemical composition of firearms propellants is provided by the propellant compounds nitrocellulose and nitroglycerine (NG). Additives that include stabilisers, plasticizers and burn modifiers are present and contribute to the compositional variation [2–5]. If partially burnt particles are located following a shooting incident examination of their physical appearance and analysis to determine their chemical profile can provide definitive evidence of a firearms origin and potential indication of a source ammunition [2–4]. Gas chromatography/mass spectrometry (GCMS) is a widely used analytical technique to determine the chemical profile of propellants [2,6,7].

Ethyl centralite and diphenylamine (DPA) are common stabilisers added to propellants. Their function is to remove nitrogen oxides produced by the degradation of nitrocellulose and nitroglycerine and so prevent autocatalytic decomposition of the propellant. DPA, the stabiliser studied in this paper, produces a range of nitro and nitroso derivatives [8–10] from the reaction with the propellant decomposition products. The reaction pathways for this process are shown in Fig. 1 with the primary reaction/degradation product being *N*-nitroso DPA (NnDPA). This compound undergoes further reactions to produce the nitrodiphenylamine (NDPA) products shown in Fig. 1. The detection of NDPAs as components of propellant can be an indicator of the level of degradation and a possible measure of age.

In the course of providing assistance to legal counsel in a matter where the analysis of firearms propellant by GCMS was involved it was noticed that phenoxazine (Fig. 2) was reported as a component of 0.22 calibre propellant that contained diphenylamine as the stabiliser [11]. No reference to phenoxazine being a component of propellant formulations could be found and it was difficult to explain as a possible by-product of the manufacturing process. The formation of this compound is also not indicated in the reaction scheme for the nitration of DPA in the cartridge case as shown in Fig. 1. While it is recognised that the elevated temperatures within the injection port of the gas chromatograph

* Corresponding author.
*E-mail address:* Hilton.Kobus@flinders.edu.au (H. Kobus).

http://dx.doi.org/10.1016/j.forsciint.2017.08.013
0379-0738/

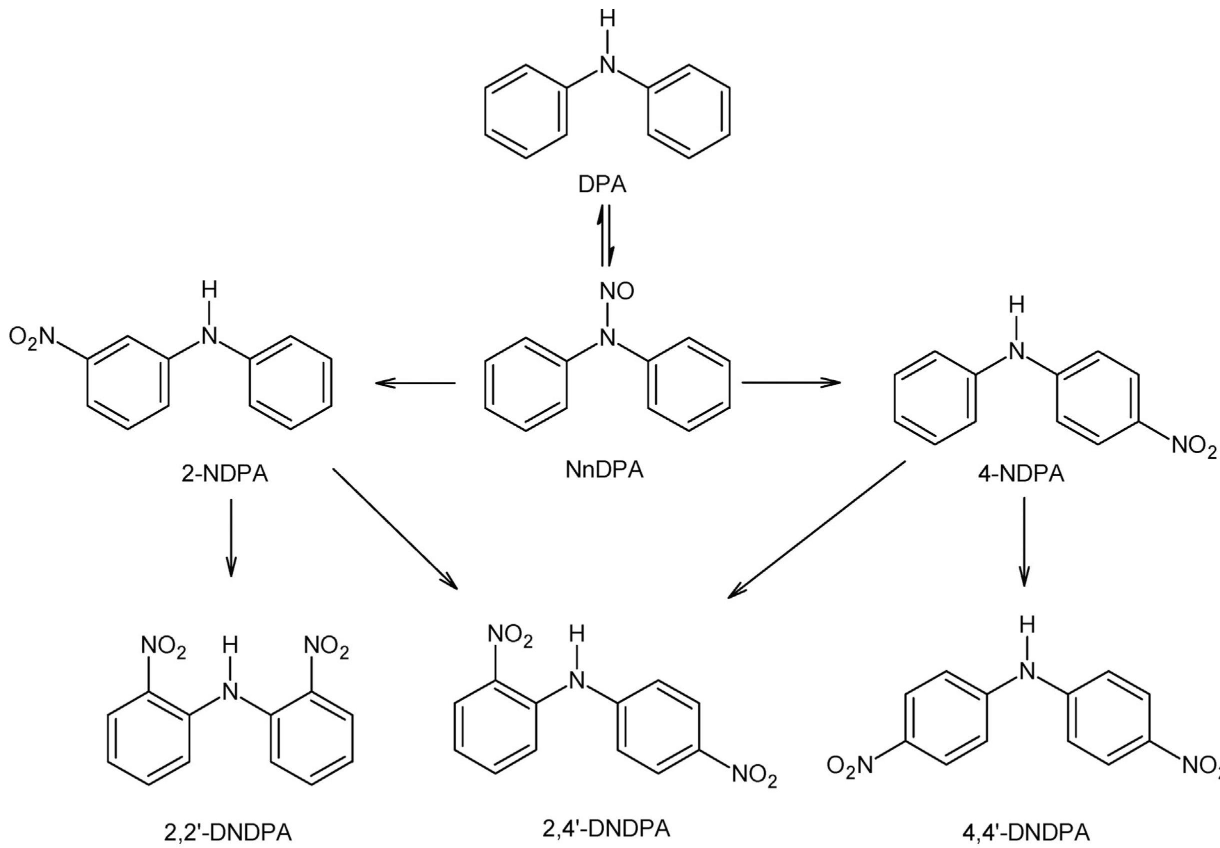


**Fig. 1.** Reaction scheme for the nitration of diphenylamine. DPA – diphenylamine, NnDP – *N*-nitrosodiphenylamine, nDPA – nitrodiphenylamine, DNDPA – dinitrodiphenylamine.

would lead to formation of the products shown in Fig. 1 [12] the possibility of the formation of other DPA-related products beside those shown in Fig. 1 should be considered. It had been noted during the course of routine work within the laboratory that the gas chromatographic profile of propellants was influenced by the cleanliness of the inlet path and this could also contribute to artefact formation.

In this paper we report on investigations undertaken to determine whether phenoxazine or other DPA related products could be formed as artefacts in the injection port of the GC.

## 2. Experimental

### *2.1. Propellant sample*

Propellant was obtained by unpacking a 0.22 rimfire cartridge of PMC (Korea) manufacture known to consist of nitrocellulose, nitroglycerine, diphenylamine (stabiliser) and dibutyl phthalate (plasticizer). GCMS analysis confirmed this composition.

### *2.2. GCMS analysis*

#### *2.2.1. Instrumentation and conditions*

Analysis was performed using an Agilent Technologies 7890A gas chromatograph with a 7693 autosampler and a 5975C mass selective detector (MSD) operated from 40 to 500 amu in electron impact (EI) mode with an ionization energy of 70 eV and source temperature of 230 °C (unless otherwise stated). Helium was used as the carrier gas at constant flow of 68 cm/s with an inlet split ratio of 20:1; the column was a 30 m × 0.25 mm × 0.25 μm HP-5 ms fused-silica capillary and the injection port was held at 200 °C (unless otherwise stated). GC conditions were (i) for the large number of sequential samples the initial column temperature was 60 °C for 2 min and then ramped at 40 °C/min to 250 °C (ii) later work investigating possible co-elution used an initial column temperature of 140 °C for 1 min and then ramped at 10 °C/min to 250 °C.

#### *2.2.2. Production of artefacts*

An attempt was made to induce the appearance of artefacts in the analysis profile due to inlet contamination through 200 injections of propellant solutions without changing the injection port

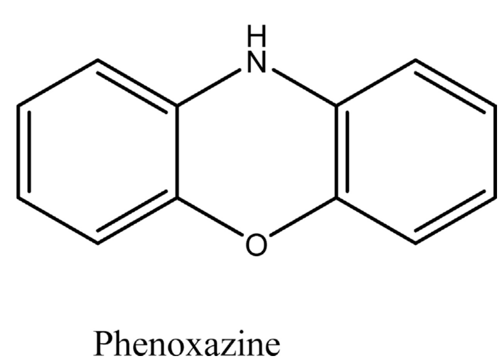


**Fig. 2.** Structure of phenoxazine.