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Assessing the evidentiary value of smokeless powder comparisons☆

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ABSTRACT

Gas chromatography–electron ionization–mass spectrometry (GC–EI–MS) and physical characteristics data for 726 smokeless reloading powders were analyzed by pairwise comparisons of samples comprising the same product and different products. Pairwise comparisons were restricted to samples having matching kernel shape, color, presence or absence of a perforation and measurements. Discrete results were analyzed for same and different products having matching chemical composition determined from a list of 13 organic components. A continuous score-based likelihood ratio was determined for same and different product comparisons using the Fisher transform of the Pearson correlation between the total ion spectra of the compared samples. Probability distributions for same product and different product comparisons appeared bimodal and were modeled with kernel density distributions. In the discrete and continuous data comparisons, the likelihood ratios for probabilities conditioned on same shape, color, presence/absence of perforation and size were found to provide relatively limited support for either the proposition of same product or different product. Further restricting the pairwise comparisons to samples belonging to the same cluster, as determined by agglomerative hierarchical cluster analysis, provided probability distributions for same product and different product comparisons that were more normal, but did not improve the resulting likelihood ratios. These results inform the forensic analyst regarding the evidentiary value of database search results and direct comparisons of recovered and control samples of smokeless powders.

1. Introduction

Smokeless reloading powders are low explosive propellants which are classified into three main categories, namely single-base, double-base and triple-base powders, depending on their energetic components. A single-base powder contains nitrocellulose as its primary energetic material, double-base powders contain nitrocellulose and nitroglycerin, and triple-base powders contain nitrocellulose, nitroglycerin and nitroguanidine [1]. In addition, smokeless powders contain a number of additional compounds which function as stabilizers, plasticizers, deterrents, flash suppressants, and opacifiers [1–3]. Single-base and double-base powders are commercially available, and can be readily purchased from sporting goods and internet retailers. The easy accessibility of smokeless powders contributes to their use in the production of improvised explosive devices (IEDs) such as pipe bombs. This work focuses entirely on the analysis of intact kernels of commercially available single- and double-base smokeless reloading powders.

Current laboratory analysis protocols for the analysis of intact smokeless powders commonly include stereomicroscopy [4], Fourier-transform infrared (FT-IR) spectroscopy [5,6], and gas chromatography–mass spectrometry (GC–MS) [7]. The forensic purposes of smokeless powder analysis have been expressed as "the identification of particles as smokeless powder and determination of product origin" [4]. The information obtained from combined chemical analysis of a smokeless powder sample, determination of its shape, color, and physical measurements has been reported in conference proceedings to allow the identification of a short list of potential manufacturers (i.e. Alliant, Hodgdon, etc.), or in some cases, a single product (i.e., Alliant 410, Hodgdon 240, etc.) from a smokeless powder database [4,8]. The combination of physical and chemical properties, in conjunction with a database search, have also been reported to allow the analyst to "uniquely identify the product" [8]. We are unaware of any reports in the peer-reviewed literature that clearly demonstrate individualization of smokeless powder products. Reported

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practices of manufacturers selling imported powders under their product names, reworking military powders and changing product formulations would complicate the individualization of powders at the product level [4,8]. Product identification by database search methods is also limited by incomplete databases [4,8]. While a database search constitutes a comparison of the physical and chemical properties of an unknown with the properties of the database records, an additional forensic question concerns whether a recovered and control sample are the same product. This paper examines the possible use of probabilistic rather than categorical statements regarding the same product designation of two intact smokeless powder samples. Results presented here are based on comparisons of records for 726 smokeless powder samples from the Smokeless Powders Database [9].

In 2009, the National Center for Forensic Science (NCFS) in collaboration with the explosives committee of the Scientific Working Group for Fire and Explosions (SWGFEX) developed the Smokeless Powders Database comprised of analytical data for commercially available single- and double-base smokeless reloading powders [9]. Methods specified by the SWGFEX explosives committee for analysis of these powders include stereomicroscopy, Fourier transform infrared spectroscopy (FT-IR), and GC–EI–MS, in addition to notation of each powder's physical characteristics. The database is comprised of contributions from a number of sources including NCFS, the Federal Bureau of Investigation (FBI), and the Netherlands Forensic Institute (NFI). The methodologies for analysis of the smokeless powders samples are available online [9]. The database is housed and maintained at NCFS, and is populated with data for each of the powders including micrographs demonstrating sample morphology (ball, cylinder, disk, etc.), color, physical measurements, FT-IR data and GC–MS data. The internet accessible database currently contains 799 records, with 726 records available for analysis at the start of this work. Additional samples are continually purchased for analysis and subsequent inclusion in the database.

Statistically based reports of smokeless powder differentiation have been published under peer-review; however, the numbers of powders examined are typically limited. Perez et al. demonstrated 100% correct classification of five smokeless powders by manufacturer using laser electrospray mass spectrometry and multivariate statistics (principal components analysis followed by k-nearest neighbors and linear discriminant analysis) [10]. In another study of seven smokeless powders by stereomicroscopy and nanoelectrospray ionization mass spectrometry (nESI-MS), it was found that several of the powders could not be discriminated by eye, but a combination of nESI-MS, extraction efficiency and microscopy allowed differentiation of all but two powders [11]. The two indistinguishable powders were different products from the same manufacturer. Keto utilized pyrolysis-gas chromatography to examine 12 smokeless powders comprising four different lots from single products arising from each of three manufacturers [12]. The pyrograms were compared based on the correlation score and the distributions of between-manufacturer and within-manufacturer correlations were found to overlap. In similar work, Andrasko used both gas and liquid chromatography to examine pre-fired powders and post-firing residues from cartridges originating from different manufacturers and different lots of the same product from a single manufacturer [13]. Correlations between the chromatographic data from pre- and post-firing powders were found to be very high and the method was suggested to be useful in determining links between shooting incidents when the gun and projectile were not available. Andrasko also suggested the possibility of determining manufacturer based on gas chromatography data, but did not demonstrate the application. These studies demonstrated differentiation of a limited number of powders, but do not provide methods for making probabilistic assertions that two smokeless powders are the same product.

This paper describes both a discrete comparison likelihood ratio and a score-based likelihood ratio calculation for pairwise comparison of intact smokeless powders with kernels having the same shape (s), color (c), presence/absence of a perforation (p) and measurement (m). These are properties that would commonly be observable in an intact powder sample and utilized, along with chemical composition, in a database search [4,8]. The discrete comparisons are based on the presence of an identical subset of 13 compounds in the two powders undergoing comparison. If the same subset of the 13 compounds is present in both powders, they are designated a "match", which supports a same product proposition, otherwise, they are designated a "non-match", which supports a different product proposition. In what is perhaps a more useful comparison of chemical composition, the distance or similarity between total ion spectra of the two samples is used as a measure of their similarity. Sample comparisons examined here were drawn from a database of 726 records. The likelihood ratio discussed here addresses propositions at the source level, where the source is defined under the prosecution's proposition, H_P, as the same product (P), with additional conditioning requirements of same kernel shape, color, etc., as described above [14,15]. Under the defense propositions, H_D, the respective statements are that the two powders are not the same product ($\bar{P}$), again with the additional conditioning requirements. Note that the term "same product" requires the same manufacturer, but may correspond to different lot numbers. A similarity score based on the Fisher transform of the Pearson correlation between the total ion spectra of two powders is calculated and designated as z. The likelihood ratios (LR) are designated as in Eq. (1).

$$LR = \frac{P(z|P, s, c, p, m)}{P(z|\bar{P}, s, c, p, m)} \quad (1)$$

2. Materials and methods

2.1. Preparation of the data

Records in the Smokeless Powders Database were donated by forensic laboratories (i.e., Federal Bureau of Investigation, Netherlands Forensic Institute, etc.) or were obtained and analyzed at the National Center for Forensic Science (NCFS), Orlando, Florida, in the United States. The samples obtained by NCFS were prepared for GC–MS analysis by extracting 10 mg of cut powder kernels in 300 μL of methylene chloride (CH_2Cl_2) over 3 h. Two separate samples of each smokeless powder were extracted and analyzed by two analysts. GC–MS analysis was conducted using a Hewlett-Packard 6890 gas chromatograph, operated in electron ionization (EI) mode, and interfaced to a 5973 mass spectrometer. The gas chromatograph was fitted with a 30 m HP-5MS (5% phenyl methyl siloxane) with a nominal diameter of 250 μm and a film thickness of 0.25 μm. An initial temperature of 40 °C was held for 1 min, followed by a temperature ramp of 25 °C min^{-1} to a final temperature of 280 °C. The final temperature was held for 3 min. Helium carrier gas was maintained at a flow rate of 1.2 mL min^{-1} on the column with an average velocity of 40 cm s^{-1}. The injection port and transfer line temperatures were 170 °C and 250 °C, respectively. In each analytical run, a 1 μL sample of smokeless powder extract was injected.

2.1.1. Limiting smokeless powder comparisons

Comparison of intact smokeless powders allows for the determination of the shape and color of the powder kernels. Some smokeless powder products contain a perforation through