



Characterization of smokeless powders using multiplexed collision-induced dissociation mass spectrometry and chemometric procedures



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ABSTRACT

This work demonstrates a non-targeted mass spectrometry approach for identification of organic compounds in smokeless powders. Unburned powders were removed from various commercial ammunitions of different brand, primer composition, caliber, and age. The unburned powders and corresponding fired residues were analyzed by liquid chromatography–atmospheric pressure chemical ionization–time-of-flight mass spectrometry (LC–APCI–TOFMS). Multiplexed collision-induced dissociation was performed at increasing collision potentials resulting in successive fragmentation that provided structural information for compound identification in a non-targeted manner. Nine compounds were identified in the powders, including akardite II, ethyl centralite, diphenylamine, *N*-nitrosodiphenylamine, and dibutyl phthalate.

Multivariate statistical procedures were performed to first investigate association and discrimination of the unburned powders. Principal components analysis (PCA) of the chemical profiles suggested nine distinct groups of powders, according to the dominant organic compounds present. The clusters formed in hierarchical cluster analysis (HCA) were mostly in agreement with PCA groupings although HCA provided a metric to quantify the similarity. Finally, association of the fired residue to the corresponding unburned powder was possible although the success was highly dependent on the composition of the unburned powder and the extent of compound depletion as a result of firing.

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1. Introduction

Smokeless powders are low explosives that constitute the propellant in ammunition cartridges [1,2]. Powders consist of the explosive material, which is typically nitrocellulose (single base) or nitrocellulose and nitroglycerin (double base), along with a series of additives that impart specific properties [2]. Among these additives are stabilizers such as diphenylamine, methyl centralite, and ethyl centralite, plasticizers such as dibutyl phthalate, and detergents such as dinitrotoluene [2]. In terms of forensic analysis, smokeless powders may be analyzed in the form of the unburned powder or as a residue after a firearm has been discharged [3–6].

Analysis of the unburned powder is necessary to determine if the powder is in fact a smokeless powder [5]. Such analysis typically involves microscopic examination to assess the morphology, physical features, and dimensions of the powder kernels, followed by instrumental analysis to determine the chemical composition of the powder [1,5,7]. Research in this area has focused on distinguishing unburned powders based on differences in organic compound profiles, typically generated using mass spectrometry methods with and without a prior separation step [8–14].

Mathis and McCord optimized an LC–MS method with electrospray ionization (ESI) to differentiate unburned smokeless powders based on their organic chemical profiles [11]. Laza et al. employed an LC–triple quadrupole (QqQ) mass spectrometer to develop a method to screen for seven organic stabilizers commonly found in smokeless powders, exploiting the multiple reaction monitoring (MRM) mode to monitor specific precursor–to-product-ion transitions [10]. Thomas et al. described an ultra-

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performance liquid chromatography tandem mass spectrometry (UPLC/MS/MS) method, using positive- and negative-ion mode ESI, as well as negative-ion mode atmospheric pressure chemical ionization (APCI), to identify 20 compounds in commercial smokeless powders [14]. Again, MRM mode was exploited to confirm the identities of powder compounds and distinction of the unburned powders was achieved based on individual compound concentrations.

Even in the absence of chromatographic separation, distinction of unburned smokeless powders based on organic composition has been demonstrated [12,13]. Scherperel et al. distinguished seven unburned powders using direct flow injection with nano-ESI and a quadrupole ion trap mass analyzer [13]. Tandem MS was performed with collision-induced dissociation (CID) energies optimized for the three common stabilizers, methyl centralite, ethyl centralite, and diphenylamine. Perez et al. generated chemical profiles of five unburned smokeless powders using laser electrospray-time-of-flight (TOF) mass spectrometry [12]. Despite a number of unidentified compounds (4–20), distinction of the five powders was achieved using principal components analysis (PCA).

In terms of residue remaining after a firearm is discharged, traditional forensic analysis involves scanning electron microscopy with energy dispersive spectroscopy to identify antimony, barium, and lead that are components in the ammunition primer. With increasing use of 'non-toxic' or 'lead-free' ammunition, there has been greater interest in characterizing the organic compounds present in the residue [15–23]. Many studies focus on characterizing the residue collected from swabs of a shooter's hands [15,16,22]. Benito et al. described a tape-lift method to collect residue from the hands after firing four non-toxic ammunitions [15]. The collected residue was analyzed by LC–quadrupole-time-of-flight (QTOF) MS and four powder additives (diethyl phthalate, 4-nitrodiphenylamine, ethyl centralite, and methyl centralite) were successfully detected in the residue. Stevens et al. analyzed hand swabs by thermal desorption GC–MS and reported the most dominant compounds in the residues were ethyl centralite and diphenylamine, which were present in 81% and 56% of swabs, respectively [22].

Rather than swab shooter's hands, the volatile compounds in spent cartridges have also been characterized with the aim of determining time since discharge [17–20]. Chang et al. used headspace solid-phase microextraction (HS-SPME) to extract volatiles from the headspace of seven spent cartridges and demonstrated time since discharge could be estimated from 1 day to more than 30 days, based on differences in abundance of diphenylamine, dibutyl phthalate, and naphthalene [18]. Gallidabino et al. described development and application of a headspace sorptive extraction (HSSE) method for the same purpose [19,20]. A total of 166 compounds were identified in nine different ammunition types, of which 141 compounds were common to all cartridges. While some of these compounds were pyrolysis products resulting from the burning process, a majority were in fact stabilizers such as diphenylamine, ethyl centralite, and akardite II [20].

While the afore-mentioned studies characterized the organic composition of the fired residue, none specifically investigated association of the residue to the unburned powder. As far as the authors are aware, there are few studies in which the composition of the fired residue and the unburned powder is compared. In separate studies, Taudte et al. and Gassner and Weyermann used UHPLC–QqQ-MS to analyze unburned powder as well as the corresponding residue collected from the shooter's hands after discharging the ammunition [23,21]. Analysis of the unburned powder was primarily used to identify the compounds likely to be present in the residue and select appropriate MRM modes for these target analytes. Neither study focused on association of the fired

residue to the unburned powder although Gassner and Weyermann did comment that while the same compounds were detected in both, differences in the relative proportions of compounds would likely preclude the ability to associate the residue to the unburned powder [21].

Further, in the majority of these studies using LC–MS methods, a targeted approach was used for compound identification, for example using a specific CID energy [13] or specific MRM modes that were pre-selected for the target analytes [10,14,21,23]. The development of a non-targeted approach would allow recognition of all compounds in a powder rather than a pre-specified set of target compounds. This has the potential to offer more informative chemical profiles that may increase discrimination among powders and enhance the ability to associate a fired residue to the corresponding unburned powder.

The work reported herein demonstrates such a non-targeted approach for the characterization of both unburned smokeless powders and the fired residue from a variety of ammunitions of different brand, caliber, primer composition, and age. Powders were analyzed by LC–TOFMS with APCI, in both positive- and negative-ion mode. This ionization method is particularly suitable for the ionization of small (less than 1000 Da) molecules of low to medium polarity and has advantages over the more commonly employed ESI for the analysis of smokeless powder constituents, such as nitrotoluenes, that lack groups that can be ionized using ESI. The non-targeted approach employed multiplexed CID, which was performed at collision potentials ranging from 10 V to 55 V in parallel spectrum acquisition [24,25]. As collision energy increases, the extent of fragmentation increases, providing structural information to allow compound identification without the need to pre-select target compounds. The resulting chemical profiles were statistically assessed using PCA and hierarchical cluster analysis (HCA) to first, evaluate discrimination of unburned powders based on chemical composition and second, to gauge the extent of association of the fired residue to the corresponding unburned powder.

2. Materials and methods

2.1. Smokeless powders

The commercial ammunitions used in this study included different brand, caliber, primer composition, and age, as shown in Table 1. The ammunitions labeled as 'new' were purchased from local stores and online suppliers within the past four years. The ammunitions labeled as 'aged' were obtained from a collaborator and were known to be at least 15 years old. Two of the aged ammunitions (PMC44A and Mag7.62A) were contained in the original packaging while the remaining three (Win12A, PMC9PbA, and CCI22A) were stored loosely in non-original packaging.

Five cartridges were selected from each ammunition and smokeless powder was removed using an inertia-based bullet puller (Lyman Magnum Inertia Bullet Puller, Lyman Products Corp., Middletown, CT). Powders from each cartridge were stored separately in scintillation vials prior to analysis. The bullet puller was rinsed with a mixture of ethanol/water (1:1, v/v) between processing of different ammunitions. For the 12-gauge samples, smokeless powders were removed by disassembling the plastic casings and transferring the powders to separate scintillation vials.

Following sample preparation guidelines described by the National Center for Forensic Science for their Smokeless Powder Database [7], 50 kernels were selected from each powder and viewed under a stereomicroscope (Nikon SMZ800, Nikon Corporation, Melville, NY, USA) connected to a digital camera (Nikon DCM1200F, Nikon Corporation). Physical features such as color, shape, luster, and perforation were recorded at 10× magnification

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