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From binary presumptive assays to probabilistic assessments: Differentiation of shooters from non-shooters using IMS, OGSR, neural networks, and likelihood ratios

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ABSTRACT

Screening tests are used in forensic science for field testing and directing laboratory analysis of physical evidence. These tests are often binary in that the data produced is interpreted as yes/no or present/absent. The utility of screening assays can be improved by evaluating a relevant background population and incorporating prior knowledge to refine the decision boundary. This paper describes the results of using ion mobility spectrometry (IMS) and hand swab samples collected from 73 individuals to differentiate shooters from non-shooters by targeting organic constituents of firearms discharge residues. Each individual completed a questionnaire helpful in analyzing positive results when they did occur. Pattern matching was undertaken using neural networks, and decision thresholds were established using likelihood ratios derived from the population study. This approach significantly reduced the background positive rates compared to an arbitrary decision threshold technique. This methodology could be extended to other pattern-recognition algorithms used with instrumental data. This paper also reports the largest population study to date focused on the organic residues of firearms discharge. The proportion of positives found in the population sample were less than 5%; when a likelihood ratio of 10:1 (shooter/not shooter) was used, the frequency of positives fell below 2%. The results suggest that background levels of organic gunshot residue will not be a significant analytic concern for assay development.

1. Introduction

When a firearm is discharged, a rich collection of physical and chemical evidence results. The discharge is initiated when the firing pin strikes and activates a shock sensitive primer which in turn ignites the propellant within the cartridge. The resulting expulsion of vapors and particles/particulates (called the plume), is a complex heterogeneous mixture referred to as firearms discharge residue (FDR). These residues are comprised of inorganic primer particulates (GSR), particles of unburnt and partially burnt propellant, and organic condensates (OGSR collectively). This complex mixture falls on surrounding surfaces including the hands, chest, shoulders, and face of the person discharging the weapon. Detecting FDR on skin does not unambiguously identify a person as a shooter, but such information is still of significant forensic interest.

Traditional analytical techniques applied to GSR such as scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM/EDS) focus on detecting the GSR formed during the flash heating and condensation of compounds from the primer. A current ASTM method describes the methodology [1]. OGSR consists of stabilizers rather than the energetics [2–7] and the most commonly studied OGSR compounds include ethyl centralite (EC), methyl centralite (MC), dimethyl phthalate (DMP), diphenylamine (DPA) and its nitration products n-nitrosodiphenylamine (N-NODPA), and 2-, and 4-nitrodiphenylamine (2NDPA and 4NDPA). A recent review describes the current status of OGSR literature [8], emphasizing mass spectrometry.

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With the evolution of new tandem and high resolution mass spectrometry, OGSR analytes are ripe for exploitation in forensic science. An additional advantage of targeting OGSR is that the analytes are amenable to screening and presumptive tests. Most screening assays, be they color-based or instrument based, produce binary (qualitative) data. With a color test for seized drugs for example, the reagent either changes color (positive) or it does not (negative). There are constraints associated with this type of assay which have been discussed and summarized in recent papers [9–15]. These considerations hold for instrumental methods of presumptive testing. In such applications, the instruments are programmed with detection thresholds above which a result is considered as positive and below which is considered as negative. Thresholds can be adjusted to minimize false negatives or false positives as the application dictates. The determination of the threshold is often arbitrary. In many screening applications, this may not be a significant concern; however, in law enforcement and security applications, it is desirable to improve assays such that results incorporate relevant prior knowledge. One way to so is through a population background study.

In this paper we report the results of a comprehensive study using ion mobility spectrometry (IMS) to screen hand swab samples for the presence of OGSR. The project included two novel features: first is the use of neural networks, probability distributions, and likelihood ratios to define criteria used to differentiate shooter swabs from non-shooter swabs. This method significantly reduced the background positive rate and could be extended to other types of binary presumptive tests. The second novel feature was the population study which included hand swab results and questionnaires from 73 individuals. Only one other paper was found discussing background concentrations of OGSR in a population [16] (six individuals). To the best of our knowledge, our work is the first population study to focus on OGSR. Results from controls and the population were used to model probability distribution functions for the neural network outputs that in turn could be interpreted as likelihood ratios. This approach significantly reduced the positive rates compared to an arbitrary decision threshold technique. This methodology could be developed for other screening assays using techniques such as IR or Raman spectroscopy in which samples are rarely pure and thus not amenable to library searching.

IMS has been successfully employed to detect the OGSR in propellants, casings, and on hand swabs [4,8,17–21]. With most portable and small bench IMS devices, samples are introduced into the instrument either by direct air sampling or by thermal desorption (TD) of a sampling fabric media. These media (referred to as swabs or wipes) can be used to sample any surface; skin is the focus of the work reported here. During IMS analysis, the TD process releases vapors into the ionization region of the instrument. Molecules are ionized using a soft ionization source such as β particles emitted from ^{63}Ni. In the ionization region, complex ion/molecule reactions occur in the presence of air to produce charged ion/molecule complexes. In the drift region of the instrument, separation occurs based on size/charge ratios. Both positive and negative ions are produced and can be detected; this project examined positive mode ions only. A mobility spectrum is a plot of intensity (mV) detected as a function of drift time (ms) which can be converted to an XY file for further processing.

One of the advantages that IMS offers for screening is the ability to detect multiple analytes simultaneously. However, IMS is based on competitive reactions at room temperature with no pre-separation prior to introduction to the drift tube. The response is thus not additive in the same sense as chromatography in which each new compound normally generates a new peak. Consequently, it is not feasible to create a peak-based detection scheme in which the software is programmed to detect multiple mobility peaks, each associated with a different component of OGSR. This problem is complicated when working with a matrix such as skin in which a wide variety of volatile organic compounds will be collected and introduced into the ionization region. This situation is neither unique to IMS nor insurmountable, but it does require the use of pattern-matching algorithms in place of peak-based methods.

In this study, three mobility patterns had to be differentiated: those arising from the hands of shooters; laboratory backgrounds and blank controls; and those arising from the hands of non-shooters. Back propagation neural networks were selected for this task. Such networks are well-suited to classification and prediction tasks across large data sets. Neural networks are considered as "machine learning" and are capable of modeling extremely complex relationships among data and variables. The network model is assumption-free and does not rely on linear or other correlations or normal distributions amongst or between variables. Because a trained network consists of a matrix of weighting factors, application to new input is instantaneous. The limitations of backpropagation networks are the tendency to "memorize" the training data at the expense of generalization. This issue can be addressed through the use of independent validation data that tests the network without being used in the training and testing process.

Neural networks are now widely used in multivariate analysis and modeling and can be implemented in many software packages, including R. A recent review describes neural networks as applied in analytical chemistry [22] and backpropagation networks in particular. Early forensic applications include optimization of instrument conditions for analysis of explosives [23] and classification of amphetamines based on GC/FTIR data [24]. Several studies reported the use of neural networks applied to forensic anthropology [25–28]. Other examples discuss applications to counterfeit pharmaceuticals [29], distance determinations in firearms examinations [30], post-mortem interval estimation [31], and identifying intoxication based on thermal imaging [32].

2. Materials and methods

2.1. Instrumentation

The ion mobility spectrometer used was a Smith's Ionscan-LS4000® which is benchtop instrument. Routine maintenance procedures recommended by the manufacturer were conducted regularly during the project. This included installing new air filter packs and membrane filters as well as cleaning the thermal desorption heaters and other accessible areas. Instruments remained powered on for the duration of the project unless errors results in the instruments being powered down or maintenance was being performed. The instruments were baked out each evening at elevated temperatures and drift flow to remove contaminants. Mobility spectra were collected upon actuation of the desorber and collected continuously for 20 s with the spectral pattern evolving across the desorption profile. A summary of instrument operating conditions is provided in Table 1. Background samples of laboratory air were analyzed at the beginning and completion of analysis and between samples to insure there was no carry-over. Blank media background samples were also obtained on a daily basis. A control chart approach was used to monitor instrument performance over time. The ion mobility spectrometers, reagents, swabs, swabbing techniques and other details have been recently published in a method validation paper [33] and a detailed report is also available on-line [34].